

# Development of High $I_c$ Ex Situ Processed YBCO Coated Conductors

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*Superconductivity for Electric Systems Annual Peer Review ♦ Washington, DC ♦ July 27-29, 2004*



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Superconductor



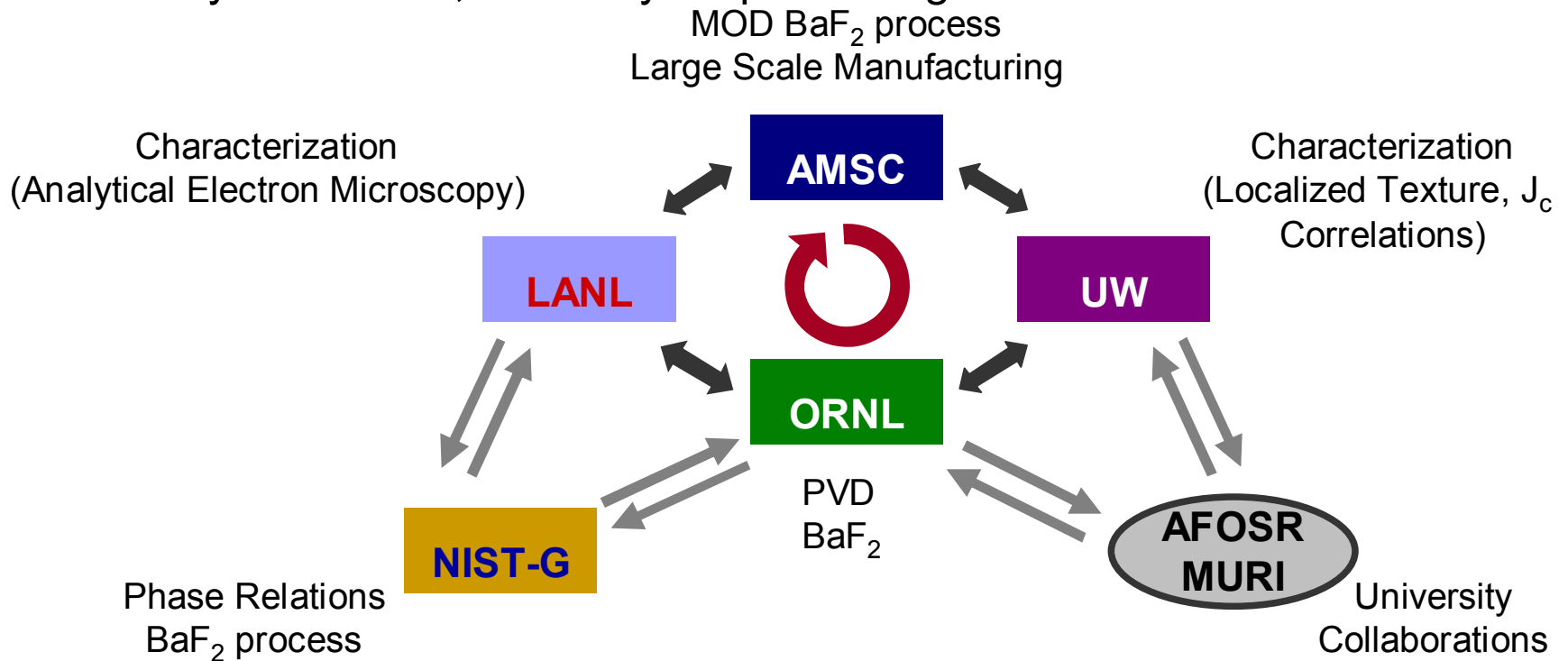
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Multi-institutional research group with the experience and expertise to focus on ex-situ processing of YBCO films.

- ❖ Grouping of existing collaborations and expertise into an effective collaboration.
- ❖ Third year of work, second year presenting at DOE annual review.



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A focused purpose and set of objectives helps guide research directions and facilitate year over year advancements.

❖ Purpose and Motivation

- To advance a materials science background for *ex situ* processing of high-performance ReBCO coated conductors
- Long-term goal: Increase  $I_c$  to 1000 A/cm at 77 K
  - consistent with 2003 DOE Coated Conductor Roadmap
  - enable broad implementation of CCs
  - reduce cost/performance ratio: \$ / kA-m

❖ Long-term objectives are to develop understanding of:

- Fundamental epitaxial growth mechanisms (*ex situ* BaF<sub>2</sub> process)
- Connectivity and the thickness dependence of  $J_c$
- Origin of flux pinning in high  $J_c$  ReBCO coated conductors

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# Several significant advancements in understanding *ex situ* YBCO film development were made in FY2004.

- ❖ Understanding of liquid phase development, laminar growth, and high- $J_c$  structures
- ❖ Grain boundary meandering and grain boundary overgrowth
- ❖ Fast processing ( $> 10\text{\AA}/\text{s}$ ) of ex-situ YBCO films
- ❖ Performance improvement year over year
  - **FY2003: 235 A/cm-w ( $J_c = 0.94 \text{ MA/cm}^2$ )** with film thickness  $2.5 \mu\text{m}$  on an ORNL RABiTS™ template.
  - **FY2004: 400 A/cm-w ( $J_c = 3.3 - 2.4 \text{ MA/cm}^2$ )** with film thickness  $1.2\text{-}1.7 \mu\text{m}$  on an AMSC RABiTS™ template.

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# Outline of Talks

- Terry Holesinger      Liquid phase formation, laminar growth, and microstructural development of high- $J_c$  *ex situ* films.
- Matt Feldmann      Through-thickness grain structure: grain boundary complexity in thick *ex situ* films
- Ron Feenstra      Processing for high  $I_c$  *ex situ* YBCO coated conductors (PVD-BaF<sub>2</sub> process).



PVD-BaF<sub>2</sub>: Physical vapor deposition of precursors



MOD-BaF<sub>2</sub>: Metal organic deposition of precursors

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# Liquid phase formation, Laminar growth, and the Microstructural Development of High- $J_c$ *ex situ* YBCO films.

Terry Holesinger

## Synopsis

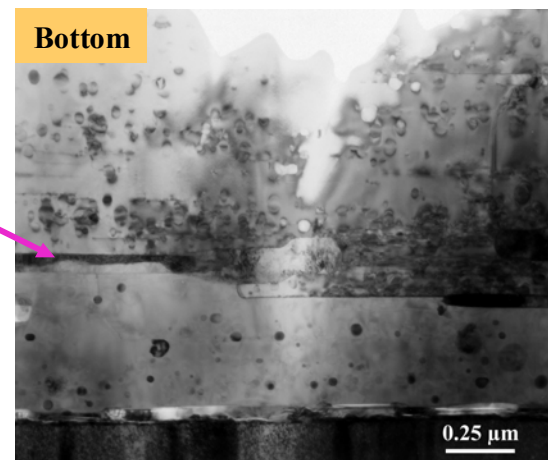
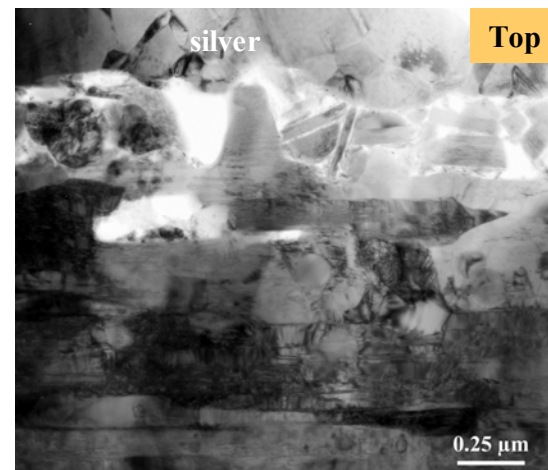
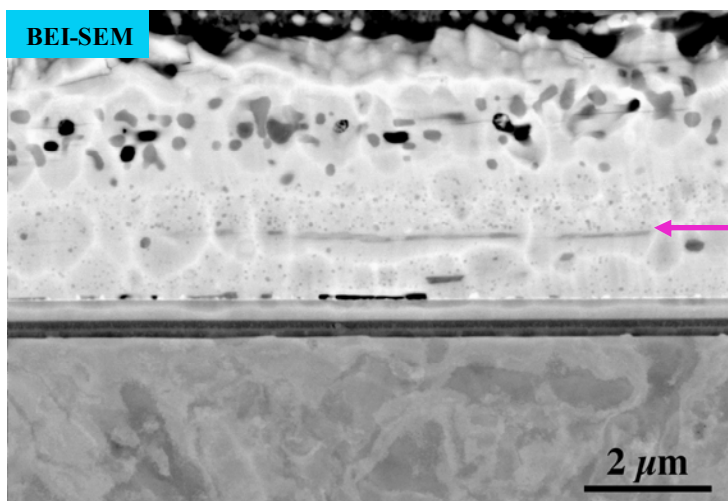
A microstructural summary is presented of a bi-modal structure in PVD-BaF<sub>2</sub> ex-situ films that forms under a certain set of standard processing conditions, the causes for its formation, and variants of this structure and their relationship to the performance level of the films.

The amount of liquid phase formation and porosity during processing plays a pivotal role in determining the microstructural uniformity, second phase assemblages, grain boundary structures, and ultimately the resulting performance levels.

Based on these insights, new processing routes have been developed that have allowed for faster conversions, uniform microstructures, and higher performance.

## The “standard” conversion of PVD-BaF<sub>2</sub> YBCO films produces high-J<sub>c</sub> films with a bi-modal microstructure.

- ❖ Bi-modal: Large, well formed YBCO grains in bottom half of film and smaller, faulted YBCO grains in the top half.
- ❖ Structure indicates two different growth modes.
- ❖ Distinguishing microstructural features.
  - Laminar growth mode.
  - Ba<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> or Ba-O-F second phase layers.
  - Large YBCO grains with layers of Y<sub>2</sub>O<sub>3</sub> precipitates.



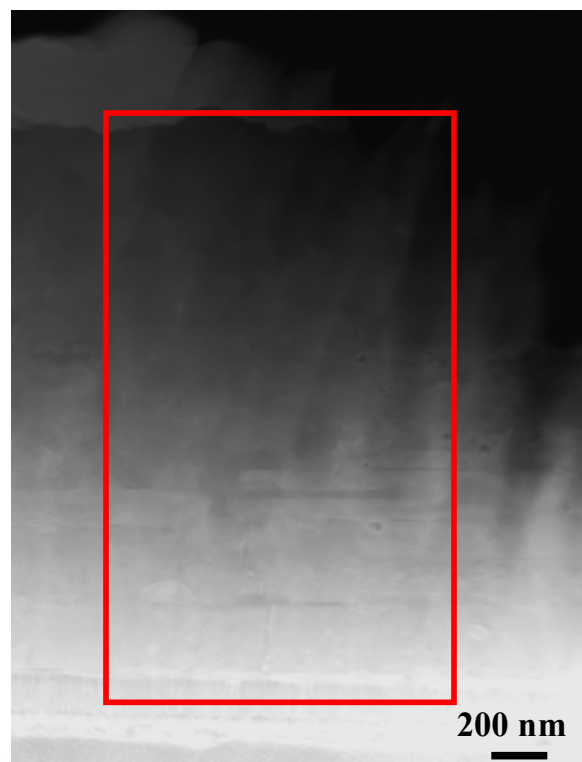
Second Phase Layers

RABiTS™ Template with **5 μm** PVD-BaF<sub>2</sub> YBCO film  
J<sub>c</sub>(77K) = 0.31 MA/cm<sup>2</sup> 155 A/cm-width

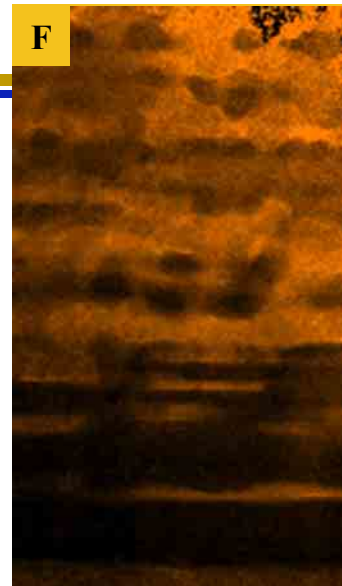
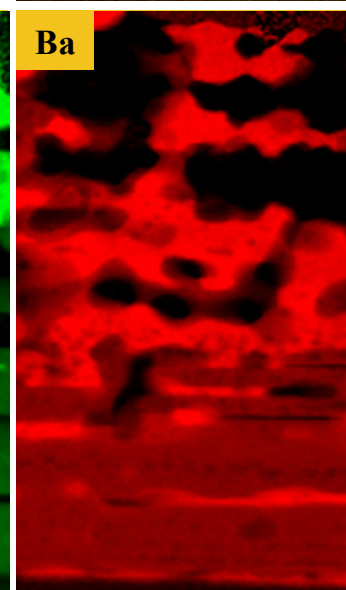
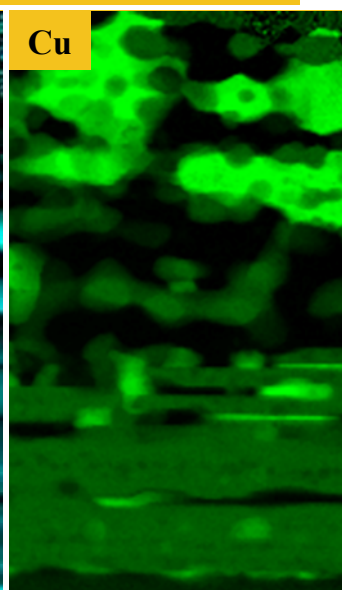
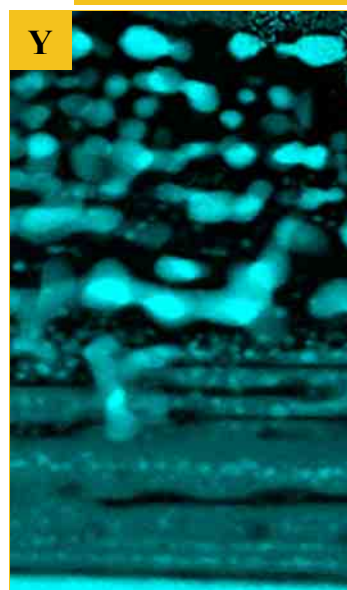
IBAD YSZ (LANL) / CeO<sub>2</sub> / BaF<sub>2</sub> YBCO (ORNL)  
J<sub>c</sub>(77K) = 0.93 MA/cm<sup>2</sup> / **2.9 μm** YBCO film / 270 A/cm-w

The bimodal structure is generated by several events that occur in the early stages of conversion.

- ❖ CuO segregation
- ❖ Excess liquid phase generation
  - $\text{Y}_2\text{O}_3$  particles floating in the Ba-O-F near growth front.
  - $(3) \text{YCuO}_x + (2) \text{Ba-O-F} \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_y + \text{Y}_2\text{O}_3$
  - Layered  $\text{Y}_2\text{O}_3$  structure within the large YBCO grains in bottom half of bimodal structure.



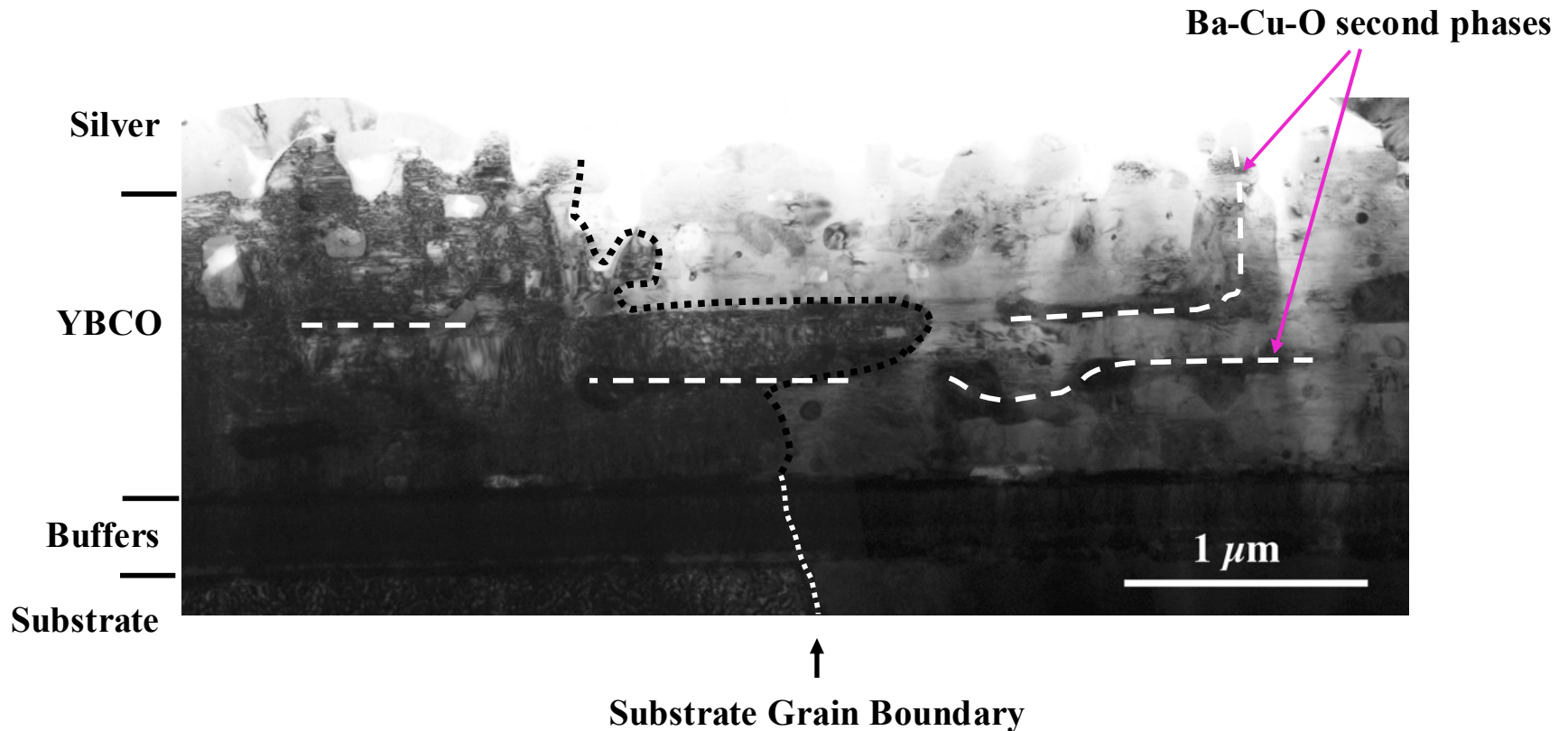
2.66  $\mu\text{m}$  film on RABiTS quenched after 1.5 hours total processing time





The laminar growth mode of *ex situ* YBCO grains manifests itself in the structures above RABiTS™ substrate grain boundaries.

- ❖ Grain boundary meandering may have important ramifications for connectivity and  $J_c$  performance levels.



## Grain boundary meandering above substrate grain boundaries also occurs in MOD YBCO films.

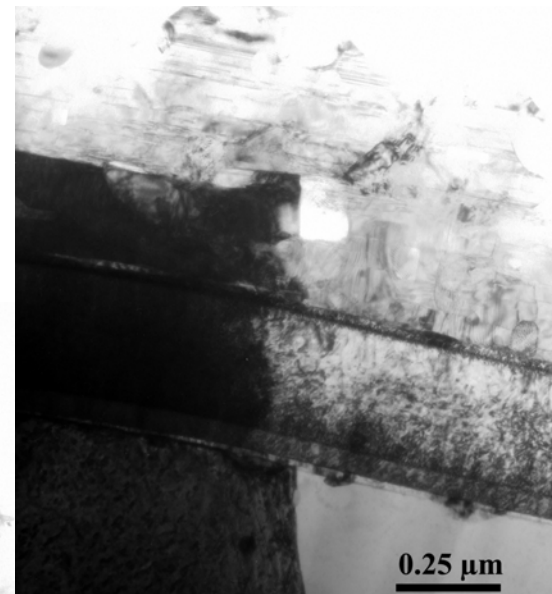
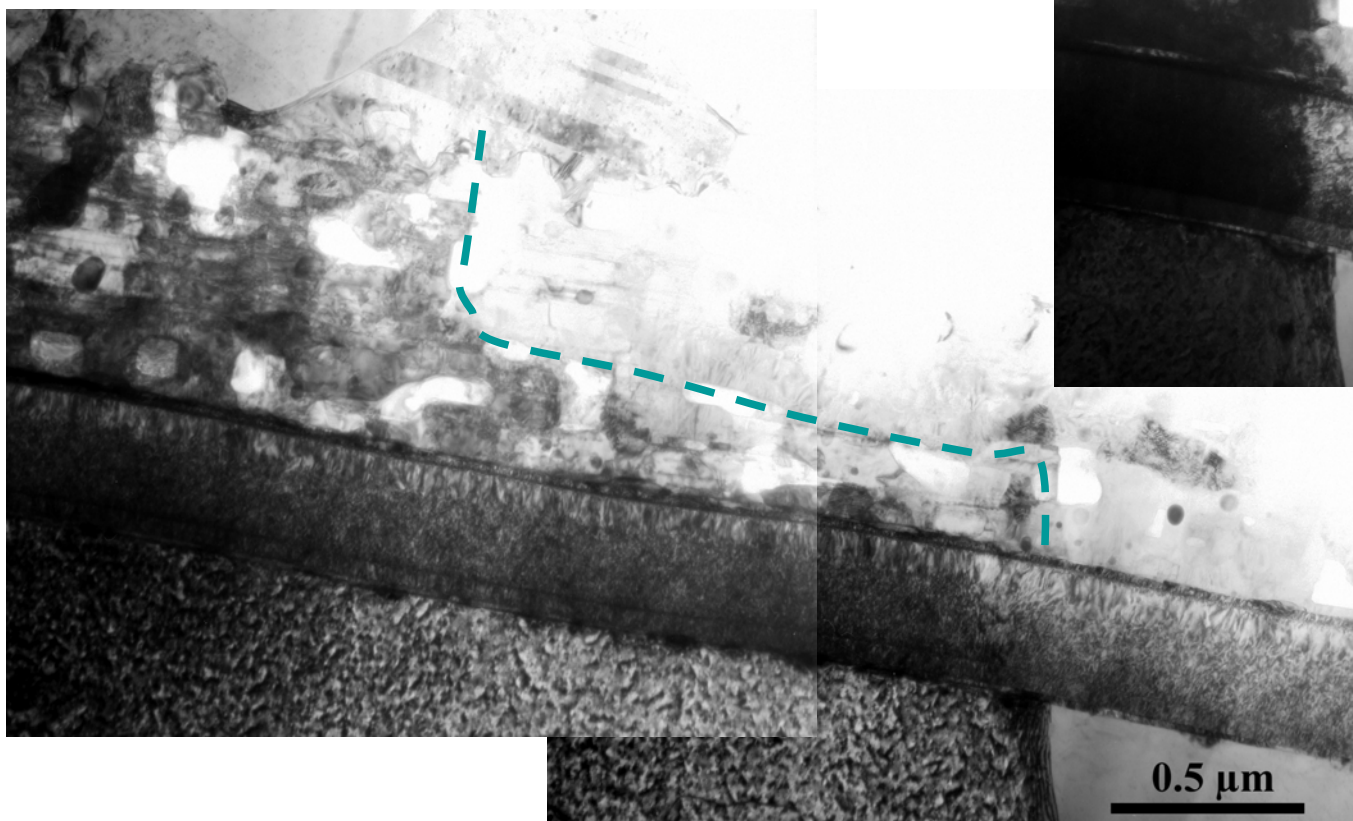
- ❖ Diffraction contrasts suggests small changes in registry can also occur within the buffer layers (right image).

Silver

YBCO

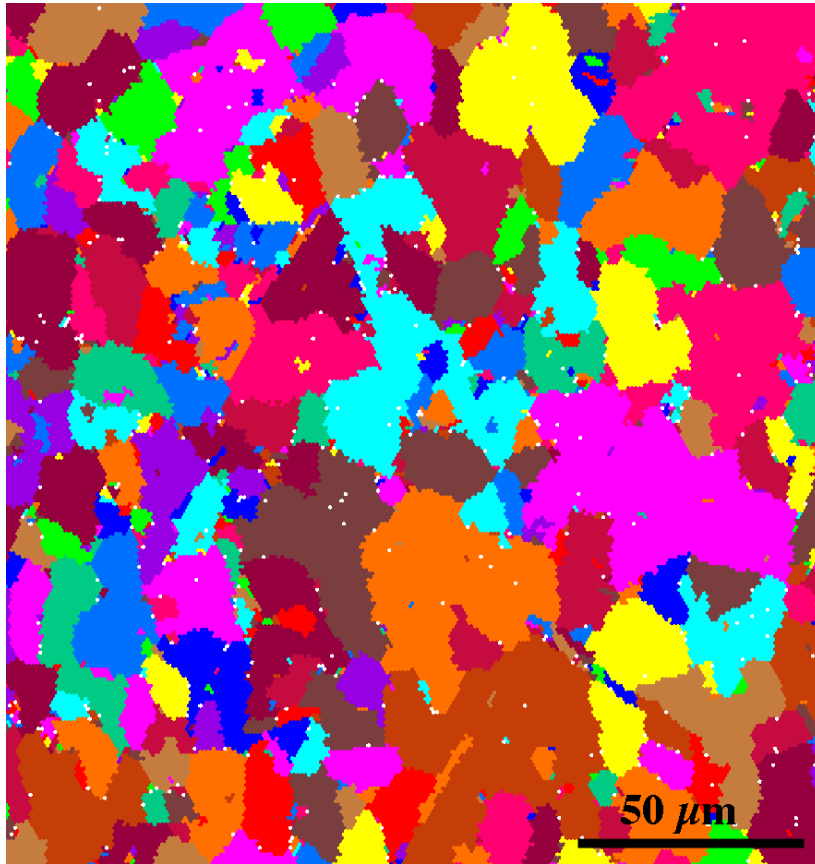
Buffer  
Layers

Substrate





Liquid phase assisted growth is evident from the large YBCO grains that can form as shown by EBSD and TEM.

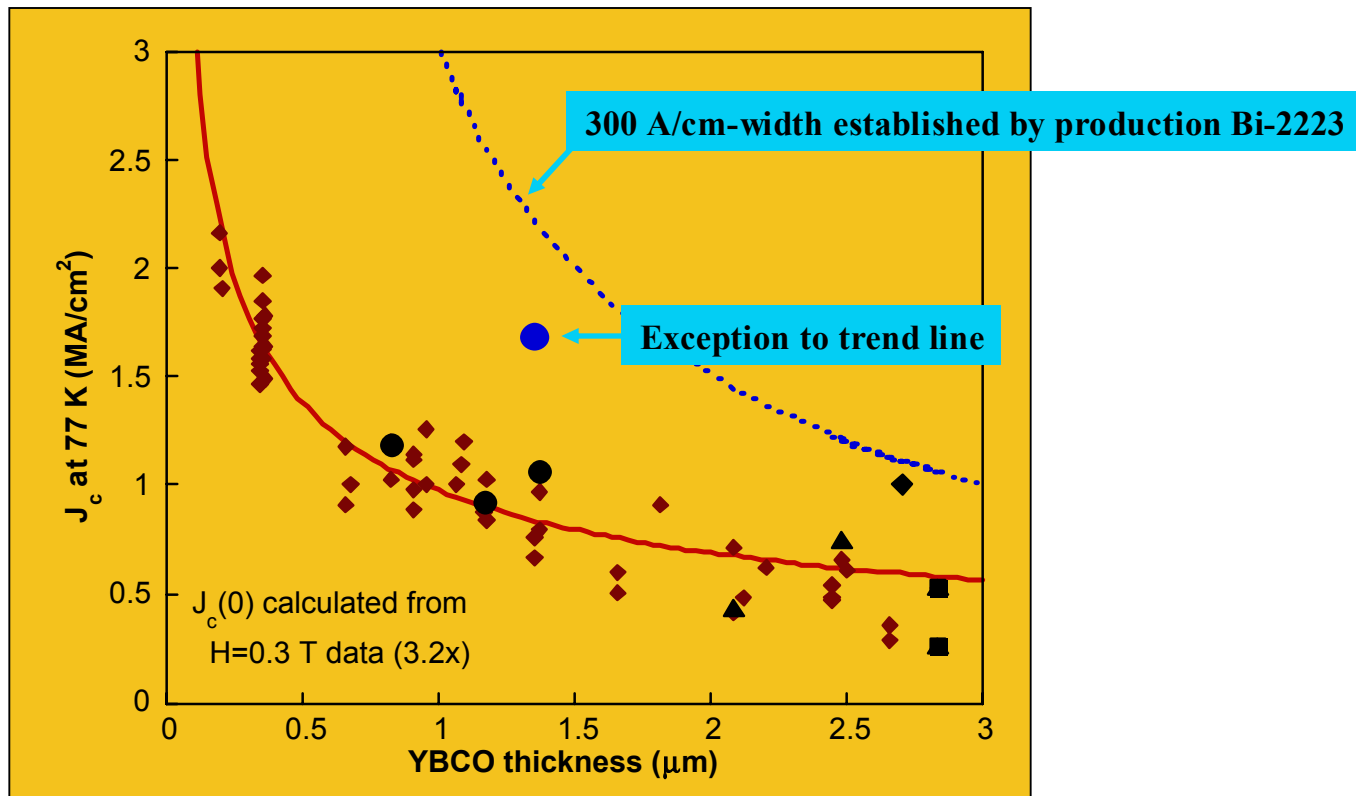


- ❖ YBCO grains up to 50 μm in size were observed by EBSD and TEM.
- ❖ The IBAD YSZ template has a grain size of  $\approx 0.1 - 0.25 \mu\text{m}$ .

IBAD YSZ (LANL) /  $\text{CeO}_2$  /  $\text{BaF}_2$  YBCO (ORNL)  
 $J_c(77\text{K}) = 0.93 \text{ MA/cm}^2$  / 2.9 μm YBCO film / 270 A/cm-w

YBCO films converted with the “standard” process (bi-modal structure) will not meet needed performance levels.

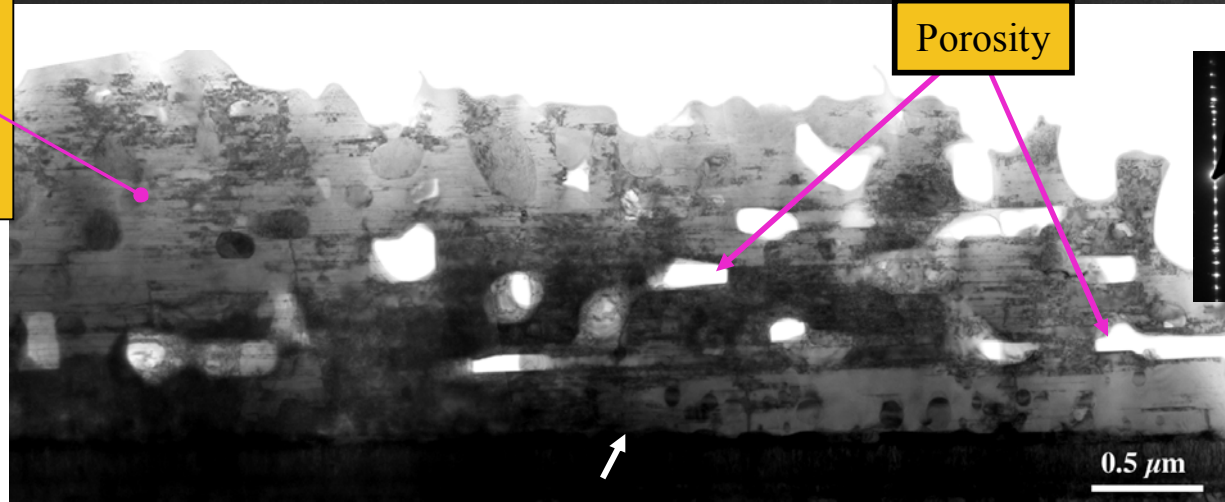
- ❖ Need to modify processing to increase  $J_c$  ( $\gg 1$  MA/cm<sup>2</sup>).
- ❖ Exceptions to the trend line were used as an opportunity to decipher the direction to take for microstructure and performance optimization.



Exceptions to the  $J_c$  trend line show variants of the bimodal structure:  
no second phase layers and reduced out-of-plane tilt.

❖ It appears that porosity plays a role in the development of high  $J_c$  microstructures.

Example 1: Bimodal structure without second phase (S.P.) layers

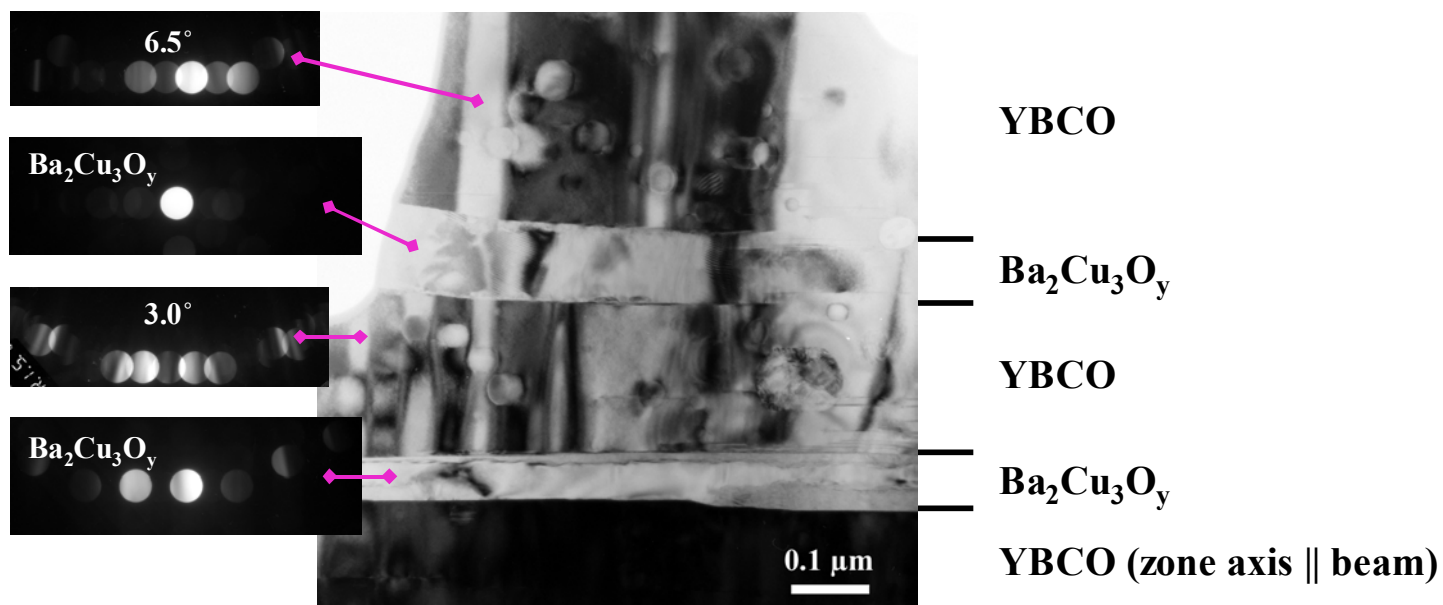


$t$ ( $\mu\text{m}$ )	$\Delta\omega_{\text{YBCO}} - \omega_{\text{YSZ}}$	$J_c$ ( $\text{A}/\text{cm}^2$ )	S.P. Layers
1.4	-0.5P	1.69	No
1.4	+0.6P	1.05	Yes
1.8	+0.6P	0.9	No
2	+1.1P	0.4	Yes

Example 2: Partial bimodal structure without second phase layers

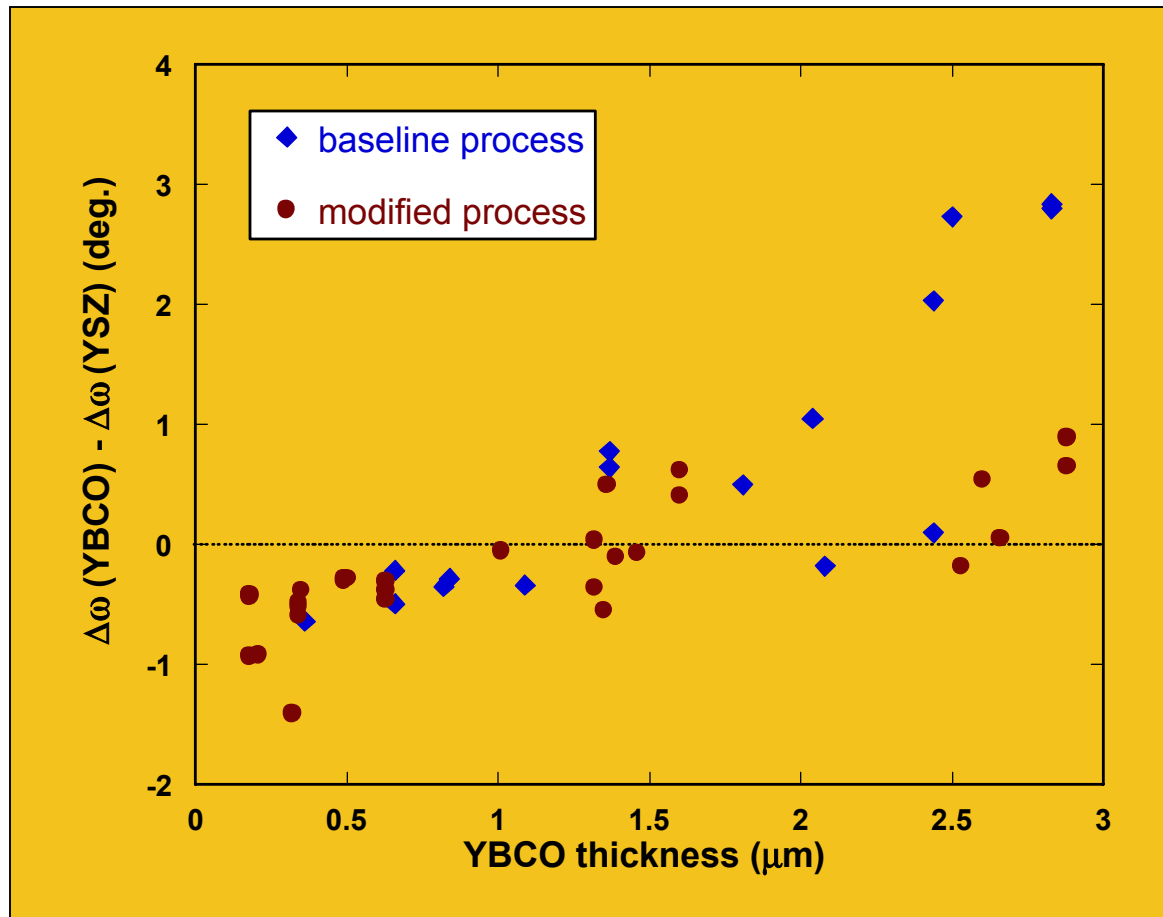
End of large grain with precipitates

Each second phase layer in a bimodal structure has the potential for YBCO alignment degradation.



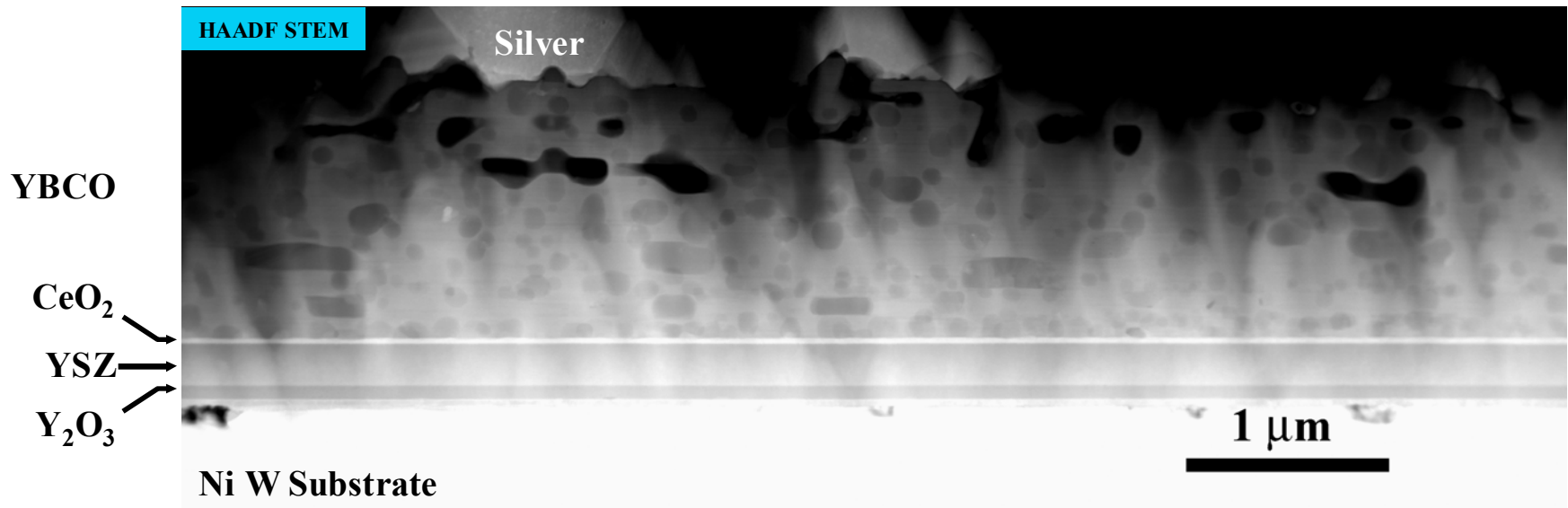
## Modified processing has demonstrated a reduced out-of-plane alignment for *ex situ* YBCO films of thicknesses greater than 1 $\mu\text{m}$

- ❖ XRD data is consistent with the reduction or elimination of second phase layers in *ex situ* YBCO films made with the modified process.



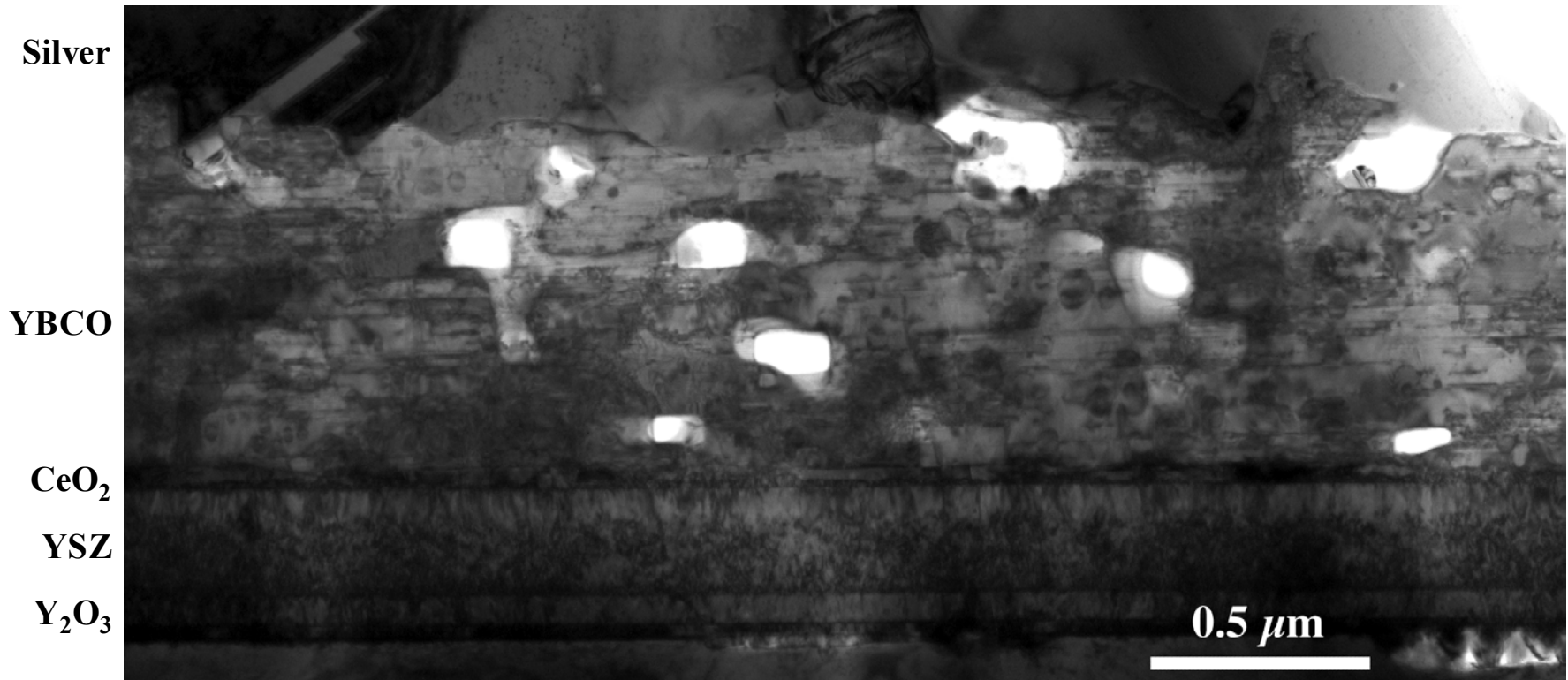
A fast modified process was developed in FY2004 to produce high- $J_c$ ,  $I_c$  films with a uniform, thru-thickness microstructure.

- ❖ Much higher performance levels  $t = 1.25 \mu\text{m}$ ,  $J_c = 2.7 \text{ MA/cm}^2$   $I_c = 334 \text{ A/cm-w}$
- ❖ New process appears to modify liquid phase generation.
  - No second phase layers
  - Porosity is present
  - Uniform distribution of planar defects and secondary phases thru thickness
- ❖ Minimized reactions with  $\text{CeO}_2$  layer.
- ❖ AMSC RABiTS template.



High performance MOD BaF<sub>2</sub> YBCO *ex situ* films have a uniform, thru-thickness microstructure.

- ❖ Uniform distribution of secondary phases and planar defects.
- ❖ No second phase layers; porosity distributed thru thickness.
- ❖ 250 A/cm-w,  $t = 0.8 \mu\text{m}$ ,  $J_c = 3.1 \text{ MA/cm}^2$



# Summary

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- ❖ Developed an understanding of the causes and effects of the bimodal microstructure.
  - Second phase layers cause misalignments and reduce  $J_c$ .
  - Variants of bimodal structure without S.P. layers allow for higher  $J_c$  values.
  - Development of a through-thickness uniform microstructure with even higher  $J_c$ 's.
- ❖ Several unique characteristics of *ex situ* grown YBCO films.
  - Laminar growth
  - Grain boundary meandering / Grain boundary overgrowth
- ❖ Currently believe that some porosity in the *ex situ* YBCO films is needed for material transport within the film during conversion. Fully dense structures may trap liquid phases leading to second phase layers.
- ❖ Samples processed by the new “fast-modified” process show uniform thru-thickness microstructures.
  - Uniform distribution of planar defects and second phases.
  - Reduced interfacial reactions with  $\text{CeO}_2$ .
  - Microstructures of high- $J_c$  MOD and PVD- $\text{BaF}_2$  films very similar.



# Outline

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- Liquid phase formation, laminar growth, and microstructural development of high- $J_c$  *ex-situ* films Terry Holesinger
- **Through-thickness grain boundary networks:  
Observation of complex GB structures in  
*ex situ* films** Matt Feldmann
- Processing for high  $I_c$  *ex situ* YBCO coated conductors (PVD  $BaF_2$  process) Ron Feenstra

# Through-thickness grain boundary networks

## Observation of complex GB structures in *ex situ* films

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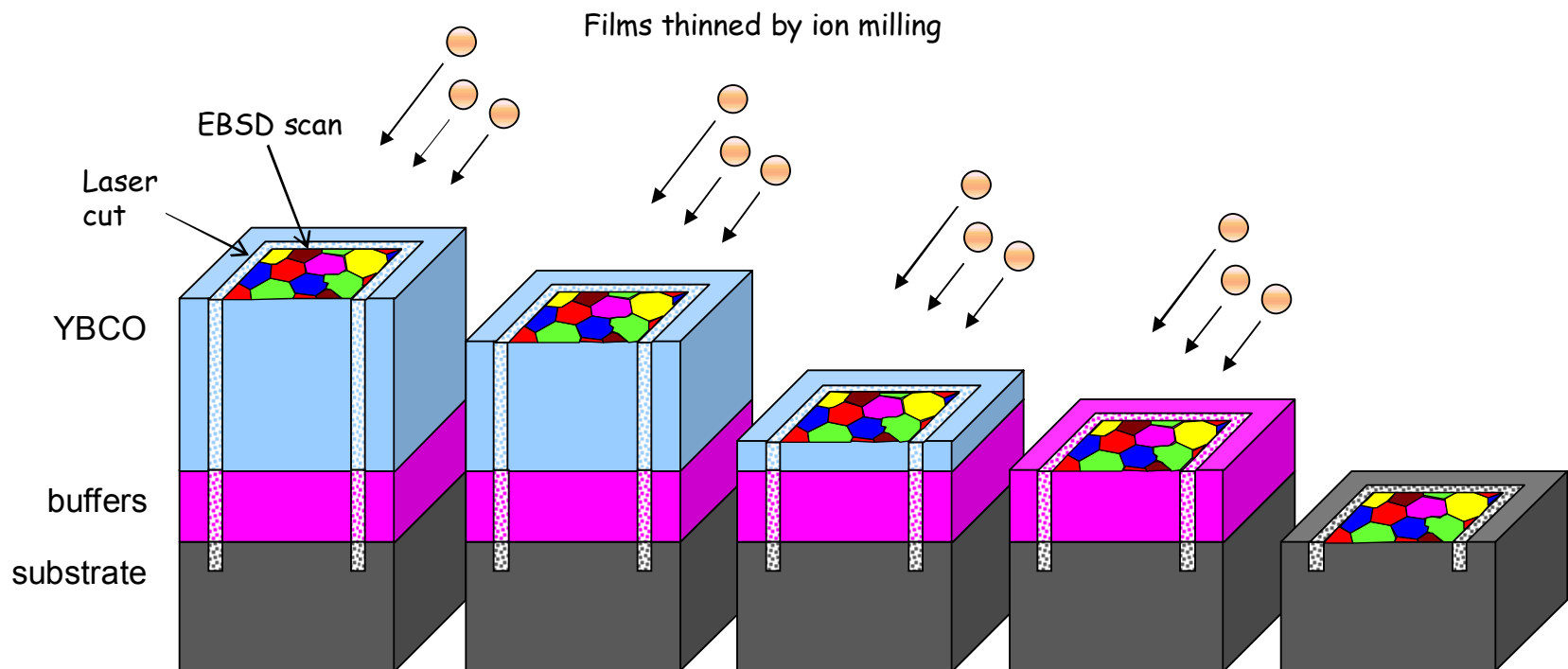
- Substrate grain boundary overgrowth
  - Result of liquid mediated growth mode
- Complex GB architecture in coated conductors
  - GB “meandering”
- Preliminary YBCO bi-crystal results
  - Investigate correlation between  $J_c$  and GB architecture

YBCO thickness	template	BaF <sub>2</sub> process	$I_c$ (A/cm)	$J_c$ (MA/cm <sup>2</sup> )
0.5 $\mu$ m	RABiTS	PVD	105	2.1
0.9 $\mu$ m	RABiTS	MOD	250	3.1
1.0 $\mu$ m	RABiTS	PVD	240	2.4
2.5 $\mu$ m	RABiTS	PVD	150	0.6
2.9 $\mu$ m	IBAD-YSZ	PVD	280	0.9

# EBSD scans through thickness provide 3D view of YBCO grain structure

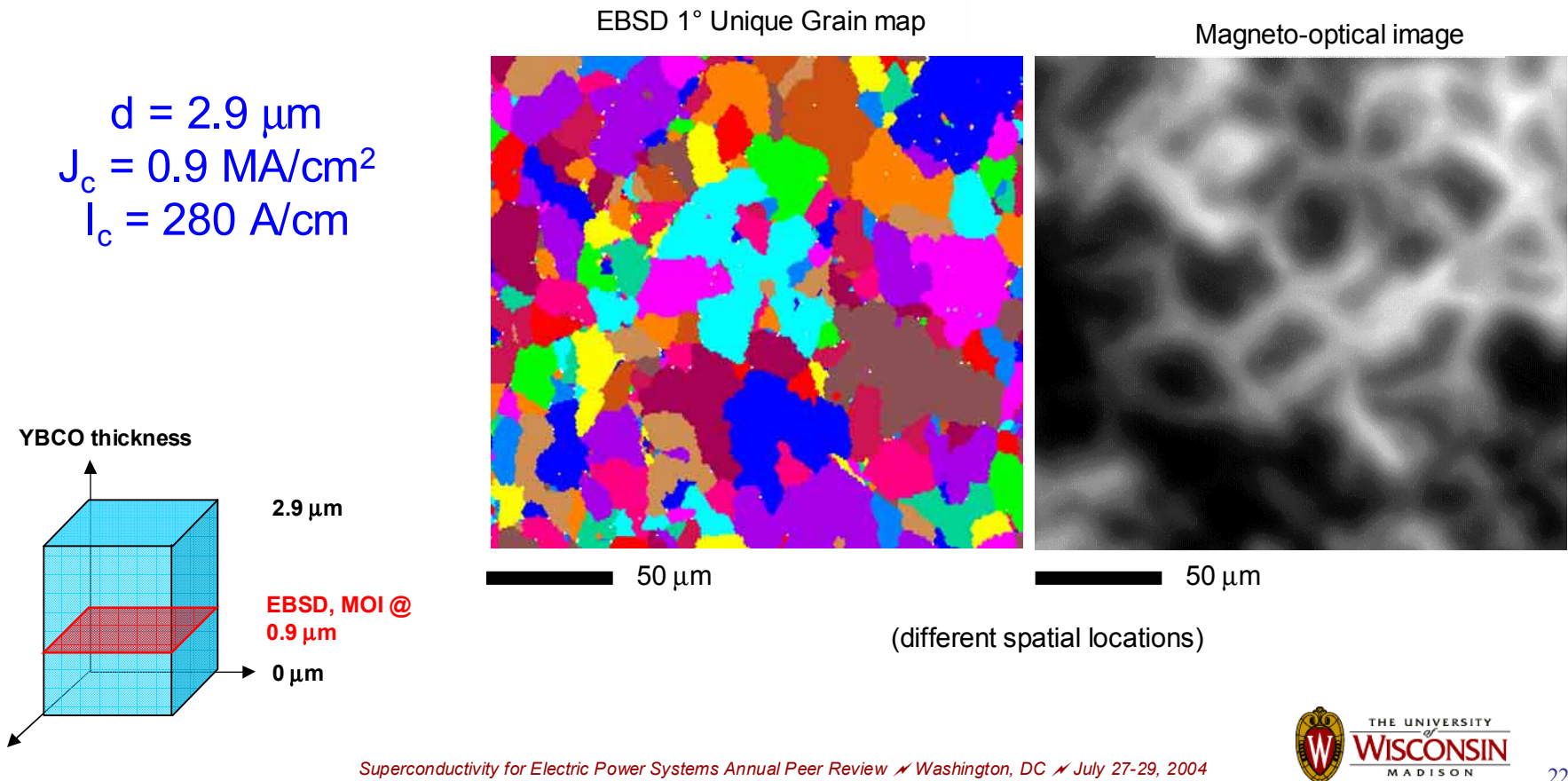
EBSD = Electron Back-Scatter Diffraction (a.k.a. EBKP, OIM)

- High quality Kikuchi patterns have been obtained from ion milled surfaces
- Laser cuts provide registration through thickness



# Liquid mediated YBCO growth mode leads to substrate grain boundary overgrowth on IBAD-YSZ

- YBCO grain size  $\sim 30\text{-}50\text{ }\mu\text{m}$ ; IBAD-YSZ grain size  $\sim 0.1\text{ }\mu\text{m}$
- YBCO grains overgrow many substrate grains and grain boundaries

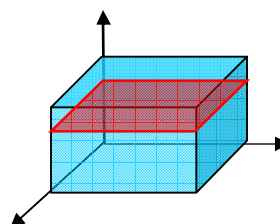
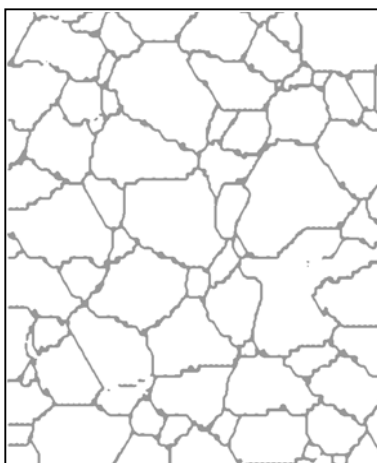
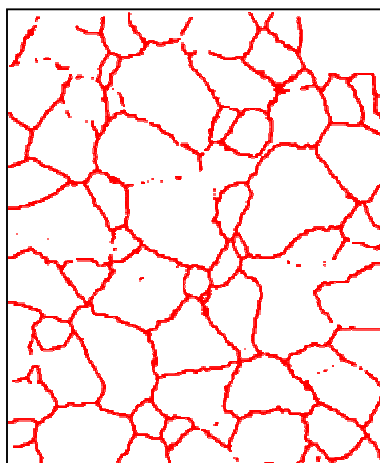


# Liquid mediated growth in thick ( $\geq 1 \mu\text{m}$ ) YBCO films also leads to substrate grain boundary overgrowth on RABiTS

$d = 0.5 \mu\text{m}$   
 $J_c = 2.1 \text{ MA/cm}^2$

YBCO  
ALL GBs  $\geq 2^\circ$

Underlying NiW  
ALL GBs  $\geq 2^\circ$

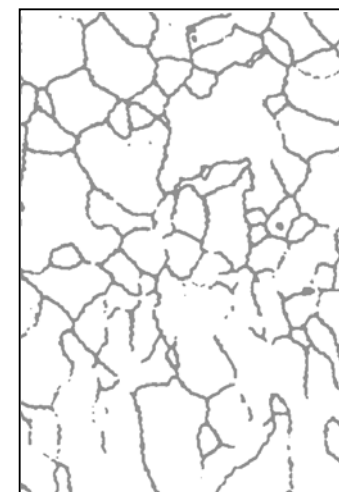
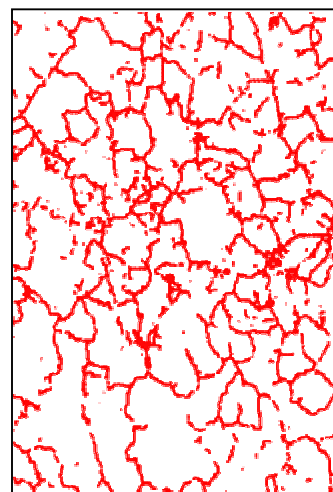


$0.5 \mu\text{m}$   
EBSD @  $0.45 \mu\text{m}$   
 $0 \mu\text{m}$

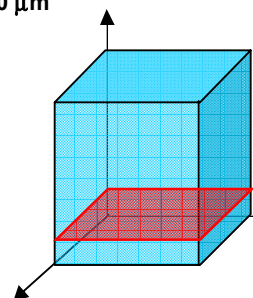
$d = 2.5 \mu\text{m}$   
 $J_c = 0.6 \text{ MA/cm}^2$

YBCO  
ALL GBs  $\geq 2^\circ$

Underlying NiW  
ALL GBs  $\geq 2^\circ$

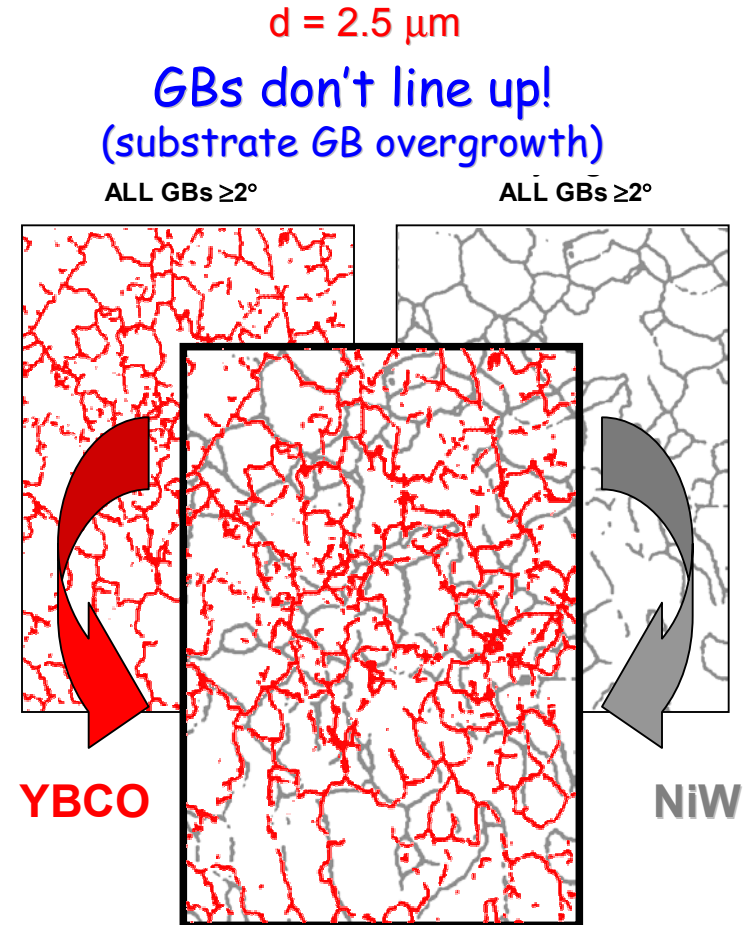
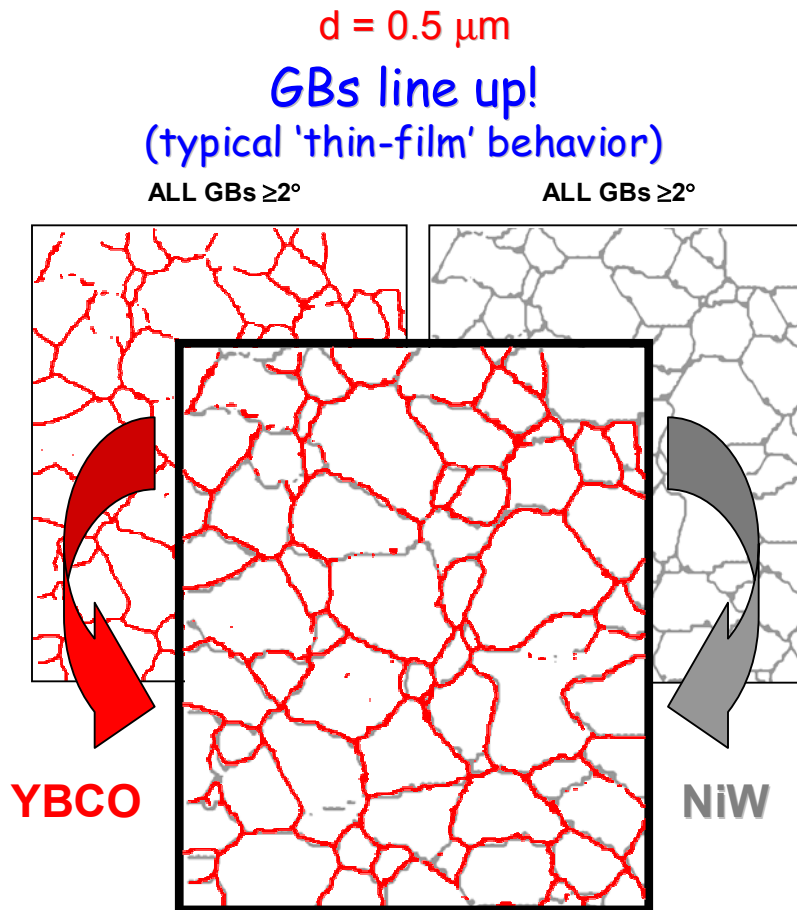


50  $\mu\text{m}$



$2.5 \mu\text{m}$   
EBSD @  $0.2 \mu\text{m}$   
 $0 \mu\text{m}$

# Liquid mediated growth in thick ( $\geq 1 \mu\text{m}$ ) YBCO films also leads to substrate grain boundary overgrowth on RABiTS



D.M. Feldmann et al, APL 77 2906 (2000)

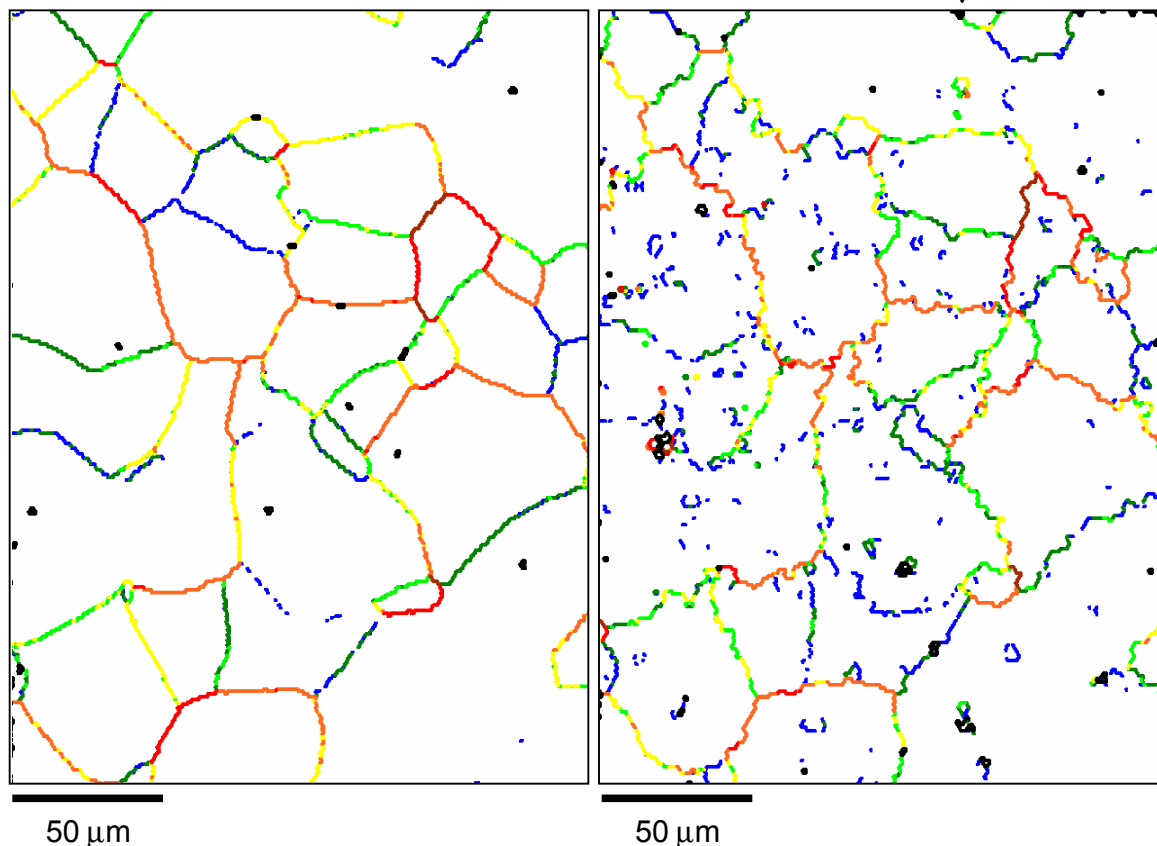
# 1.0 $\mu\text{m}$ thick “fast process” YBCO film shows intermediate role of liquids — GB meandering

- YBCO: substrate grain structure is recognizable, but GBs “meander”

$J_c = 2.4 \text{ MA/cm}^2$   
 $I_c = 240 \text{ A/cm}$   
RABiTS

YSZ

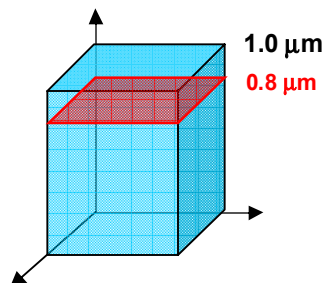
YBCO 0.8  $\mu\text{m}$



GBs color coded by total misorientation angle ( $\theta$ ):

	Min	Max
Blue	2°	3°
Dark Green	3°	4°
Light Green	4°	5°
Yellow	5°	6°
Orange	6°	8°
Red	8°	10°
Brown	10°	15°
Black	15°	180°

YBCO thickness





# GB meandering is reproducible under different scan conditions

Very similar meander observed for both scan conditions



1.0  $\mu\text{m}$  step size  
Beam Energy = 30 kV



0.6  $\mu\text{m}$  step size  
Beam Energy = 20 kV

(~70% smaller YBCO volume sampled at each point\*)

\*A. Goyal et al, *Micron* **30** 463 (1999)

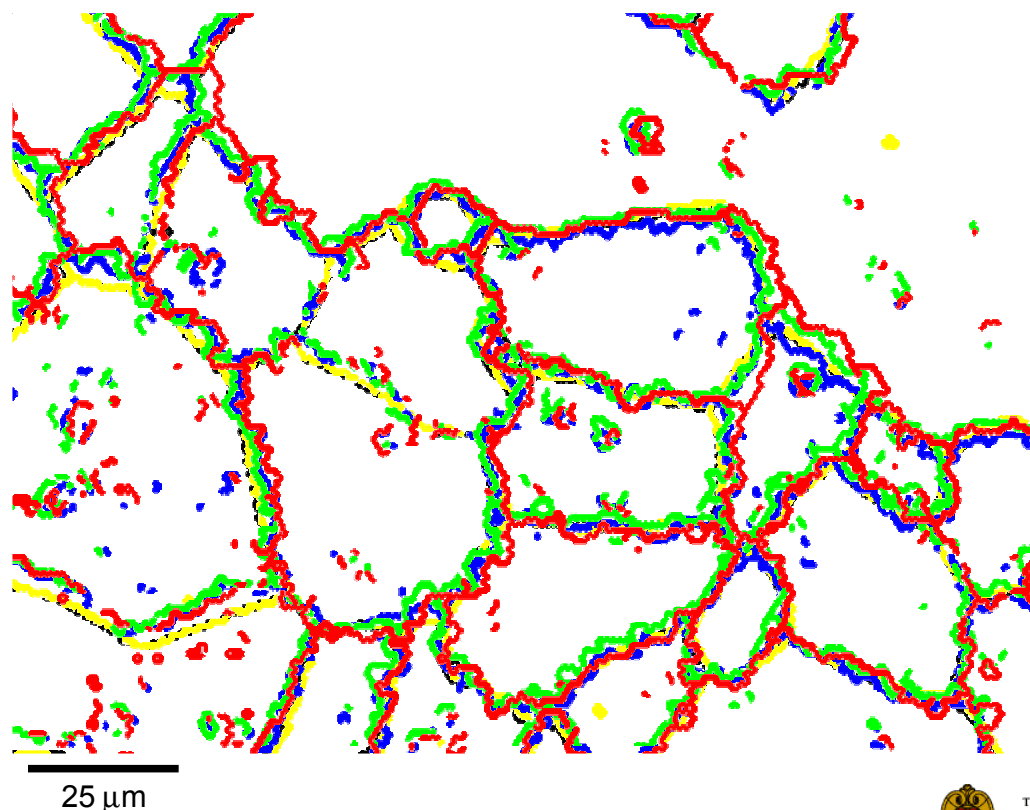
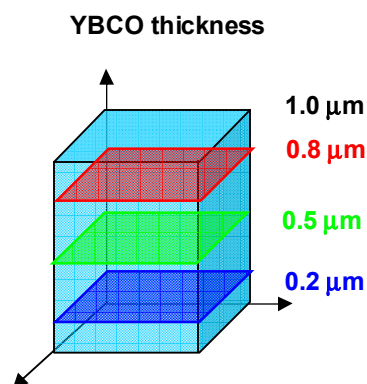


# 1.0 $\mu\text{m}$ thick "fast process" YBCO film shows significant plan-view and through-thickness GB meandering

- $\theta$  remains constant through thickness – Meandering increases GB area

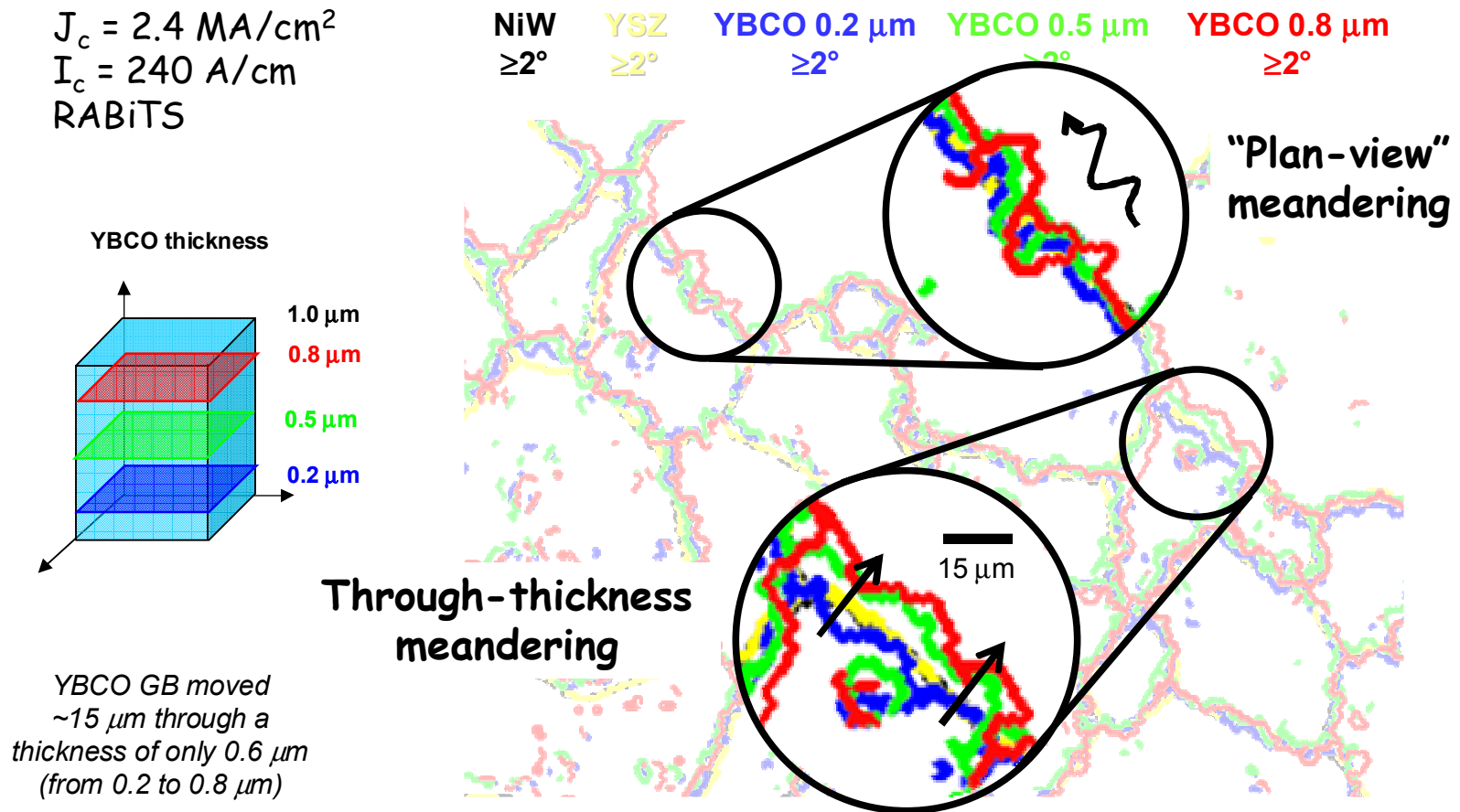
$J_c = 2.4 \text{ MA/cm}^2$   
 $I_c = 240 \text{ A/cm}$   
RABiTS

NiW  $\geq 2^\circ$     YSZ  $\geq 2^\circ$     YBCO 0.2  $\mu\text{m}$   $\geq 2^\circ$     YBCO 0.5  $\mu\text{m}$   $\geq 2^\circ$     YBCO 0.8  $\mu\text{m}$   $\geq 2^\circ$



# 1.0 $\mu\text{m}$ thick "fast process" YBCO film shows significant plan-view and through-thickness GB meandering

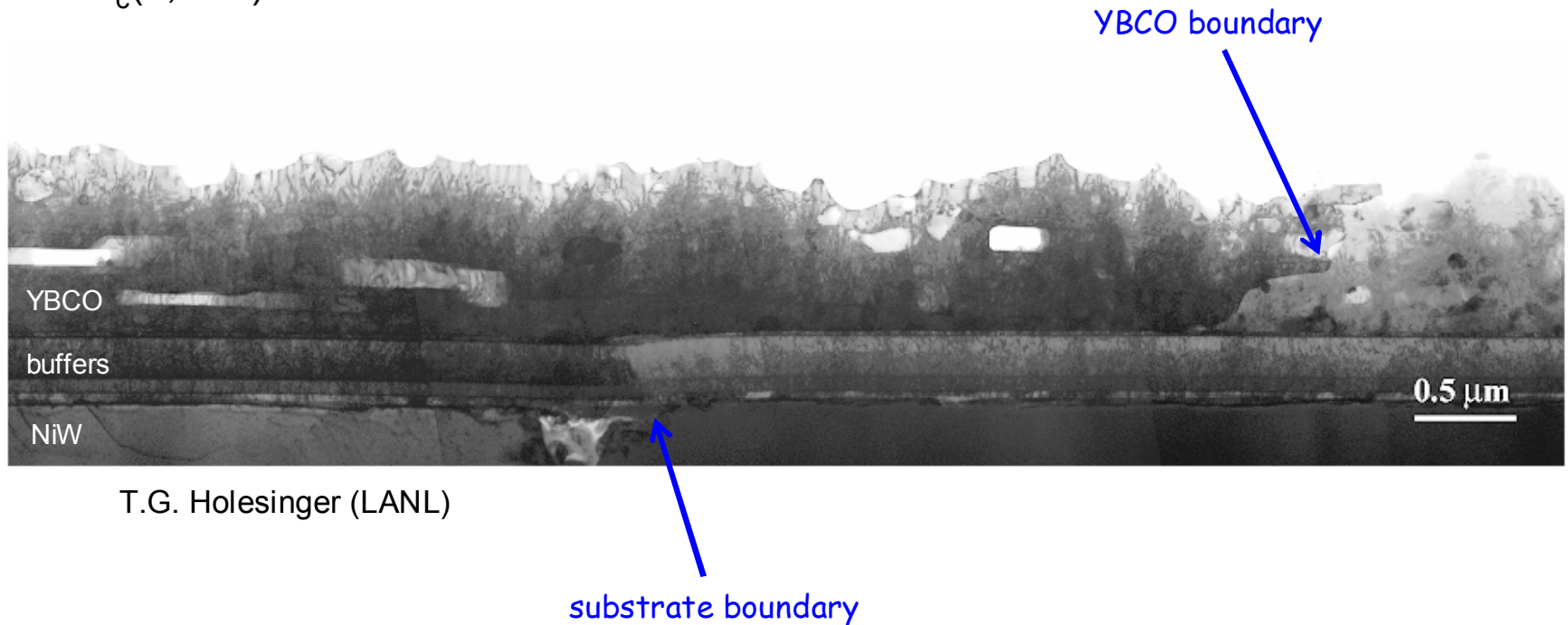
- $\theta$  remains constant through thickness – Meandering increases GB area



# Substrate GB overgrowth and through-thickness meandering also observed with x-sec TEM

$d = 1.25 \mu\text{m}$

$J_c(0, 77\text{K}) = 2.7 \text{ MA/cm}^2$



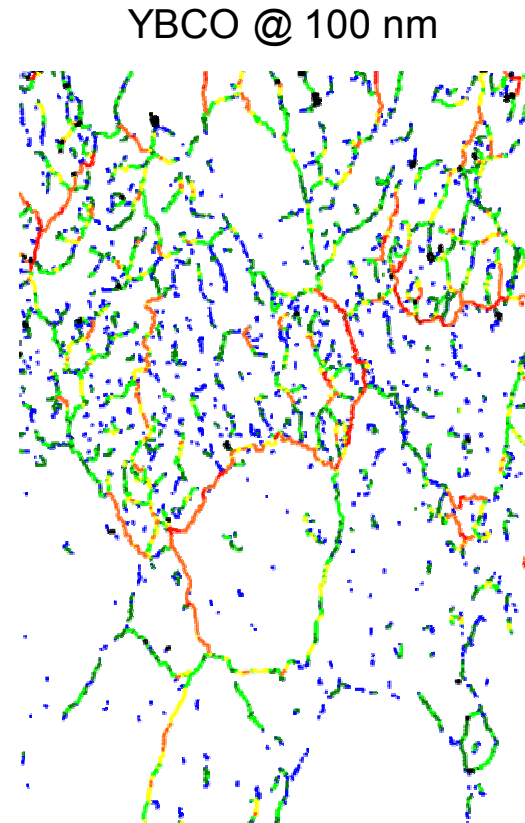
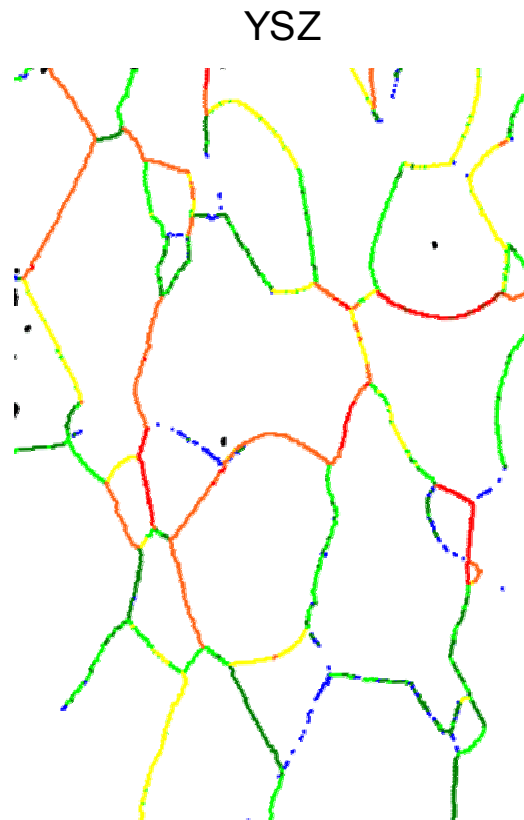
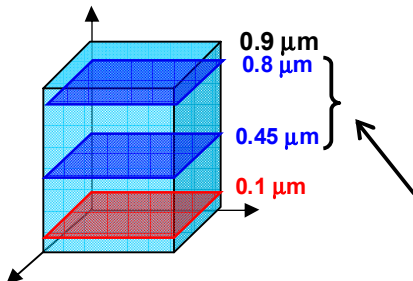
# MOD BaF<sub>2</sub> process films on RABiTS exhibit GB meandering and a YBCO "sub-grain" structure

➤ Both plan-view and through thickness meandering observed, but more pronounced in PVD films

➤ Additional YBCO sub-grain structure found



$J_c = 3.1 \text{ MA/cm}^2$   
 $I_c = 250 \text{ A/cm}$   
RABiTS



GBs color coded by total misorientation angle ( $\theta$ ):

	Min	Max
Blue	2°	3°
Green	3°	4°
Light Green	4°	5°
Yellow	5°	6°
Orange	6°	8°
Red	8°	10°
Brown	10°	15°
Black	15°	180°

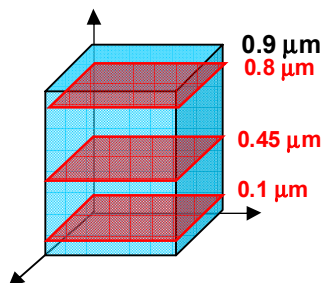
EBSD (not shown) also shows through-thickness GB meandering

# MOD BaF<sub>2</sub> process films on RABiTS exhibit GB meandering and a YBCO "sub-grain" structure

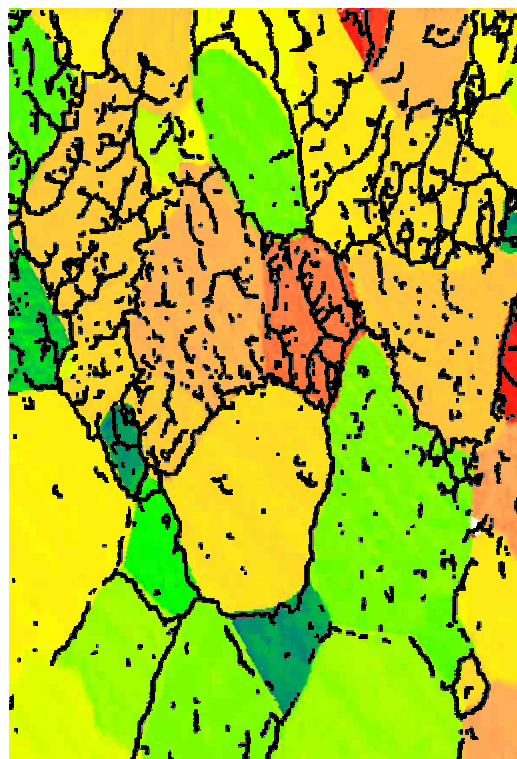
➤ Sub-grain structure appears above substrate grains with greater out of plane tilt



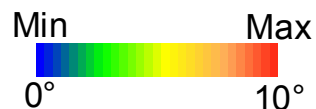
$J_c = 3.1 \text{ MA/cm}^2$   
 $I_c = 250 \text{ A/cm}$   
RABiTS



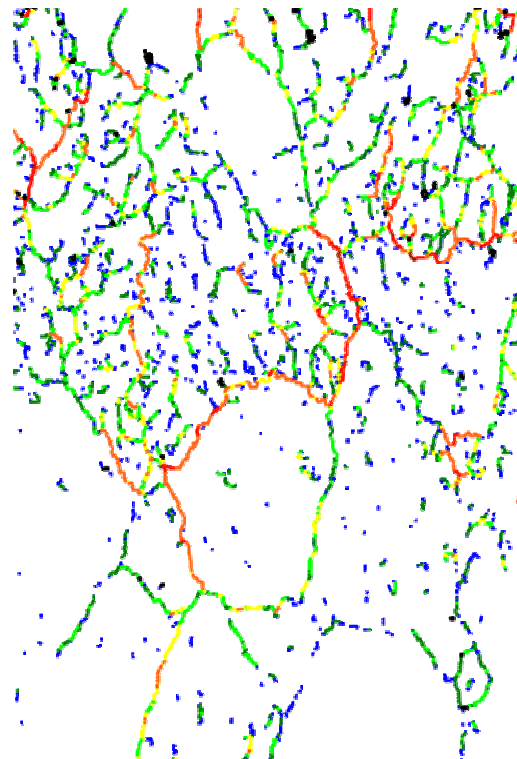
YSZ *out of plane orientation*



40  $\mu\text{m}$



YBCO @ 100 nm



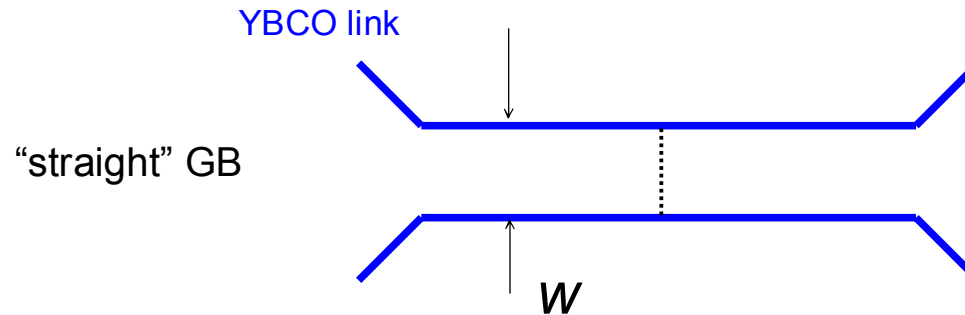
40  $\mu\text{m}$

GBs color coded by total misorientation angle ( $\theta$ ):

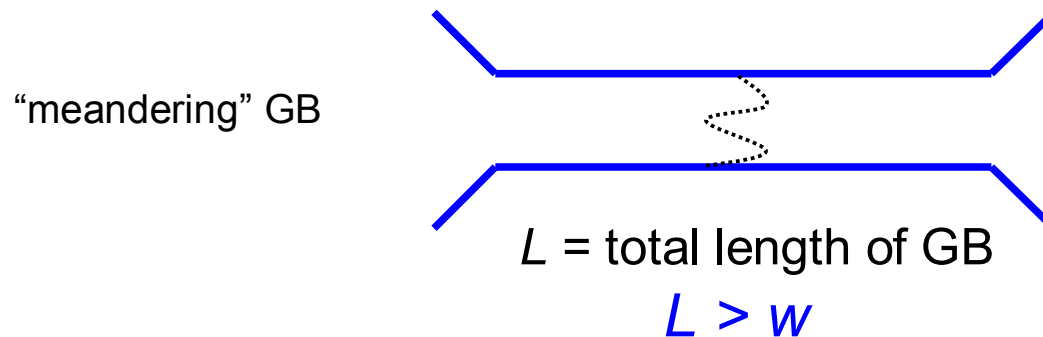
	Min	Max
Blue	2°	3°
Green	3°	4°
Yellow	4°	5°
Orange	5°	6°
Red	6°	8°
Dark Red	8°	10°
Black	10°	15°
Black	15°	180°

*Angle between sample normal and nearest crystal axis*

# Does an increased GB area result in a higher $I_c$ ?



$$I_c = J_c(\text{GB}) \times w \times d$$



$$I_c \sim J_c(\text{GB}) \times L \times d ??$$

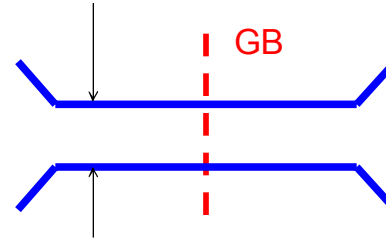
# Bi-crystal experiment motivated by observation of GB meandering in CCs

❖ YBCO films grown by PLD ( $d = 0.18 \mu\text{m}$ )

❖  $5^\circ$  STO bicrystal substrates (no buffers)

❖ Width of links held fixed at  $50 \mu\text{m}$

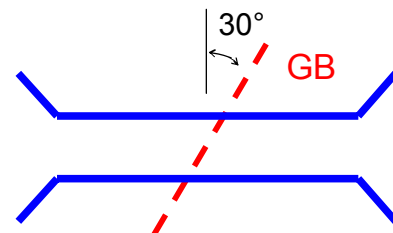
$w = 50 \mu\text{m}$



“straight” GB

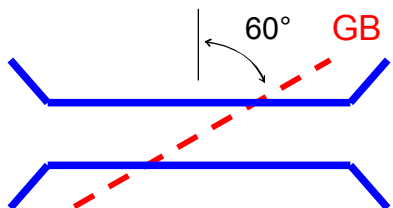
*GB length*

$w$



$30^\circ$  tilt

$1.15 w$



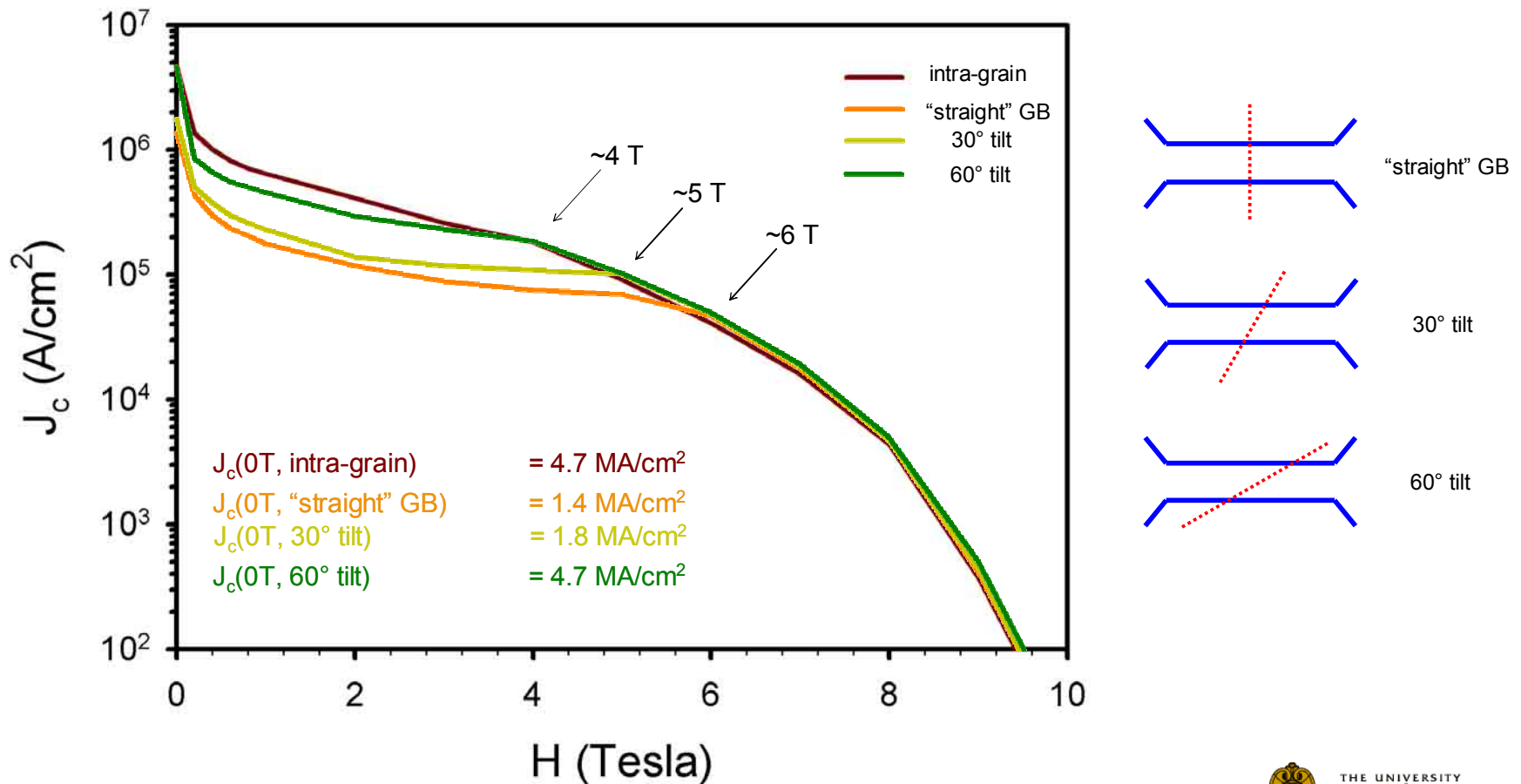
$60^\circ$  tilt

$2 w$



# Oblique GBs result in a higher link $J_c$

- Increasing the GB area appears to improve the transparency of the GB to transport current





# Summary

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- Liquid mediated growth mode allows YBCO to overgrow substrate GBs
- The different roles of liquids in *ex situ* films produce different grain and GB geometries
  - $d = 0.5 \mu\text{m}$  “straight” GBs – *reduced role of liquids*
    - YBCO GBs overlap substrate GBs
  - $d = 1.0 \mu\text{m}$  “meandering” GBs – *intermediate role of liquids*
    - YBCO GBs meander along substrate GBs
  - $d = 2.5 \mu\text{m}$  large substrate GB overgrowth – *excessive liquid growth*
    - Almost complete disconnect between YBCO and substrate GBs
- Complex GB architecture observed in CCs
  - “plan-view” and through-thickness GB meandering discovered
  - Bi-crystal experiment suggests a relationship between GB area and overall  $J_c$
  - $\theta$  alone is insufficient to describe the transport properties of GBs in CCs

# Outline

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- Liquid phase formation, laminar growth, and microstructural development of high- $J_c$  ex-situ films Terry Holesinger
- Through-thickness grain boundary networks: Observation of complex GB structures in *ex situ* films Matt Feldmann
- **Processing for high  $I_c$  *ex situ* YBCO coated conductors (PVD  $BaF_2$  process)** Ron Feenstra

# Processing for high $I_c$ ex situ YBCO coated conductors (PVD-BaF<sub>2</sub> process)

## FY2004 milestones

- **obtain 10 Å/s growth rate with PVD-BaF<sub>2</sub> precursors**
  - equivalent duration: 17 min /  $\mu\text{m}$
  - previously: 2-3 h /  $\mu\text{m}$  (“standard” process)
- **increase  $I_c$  on CC substrates to values > 400 A/cm (77 K)**
  - previous best values:
    - 235 A/cm 2.5  $\mu\text{m}$  YBCO on Ni-W RABiTS (ORNL)
    - 280 A/cm 2.9  $\mu\text{m}$  YBCO on IBAD-YSZ (LANL)
- Added task related to participation in the CC-WDG (since 12/2003):  
“study origin of and improve flux pinning in PVD-BaF<sub>2</sub> conductors”

# Strategies to increase $I_c$

- “lean and mean”

increase  $J_c$  for intermediate 1-1.5  $\mu\text{m}$  thickness range  
+ AMSC has realized large gains in  $I_c$  of 1  $\mu\text{m}$  YBCO  
by process improvements

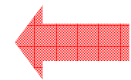
- “brute force”

produce thick YBCO coatings:  $d > 2 \mu\text{m}$   
+ unique opportunities for PVD-BaF<sub>2</sub> process  
+ irreversible strain limit  $\epsilon_{\text{irr}} > 0.4\%$  in 2.75  $\mu\text{m}$  YBCO  
on Ni-5%W RABiTS (NIST-Boulder, this Review)  
– limited overlap with MOD

- “smart”

study origin of thickness dependence of  $J_c$   
+ focus of work in FY2003

FY2004



# “Killing two birds with one stone”

Central to the progress in FY2004 was the development of  
a **fast process** yielding **higher  $I_c$**   
than “standard” (slow) processing

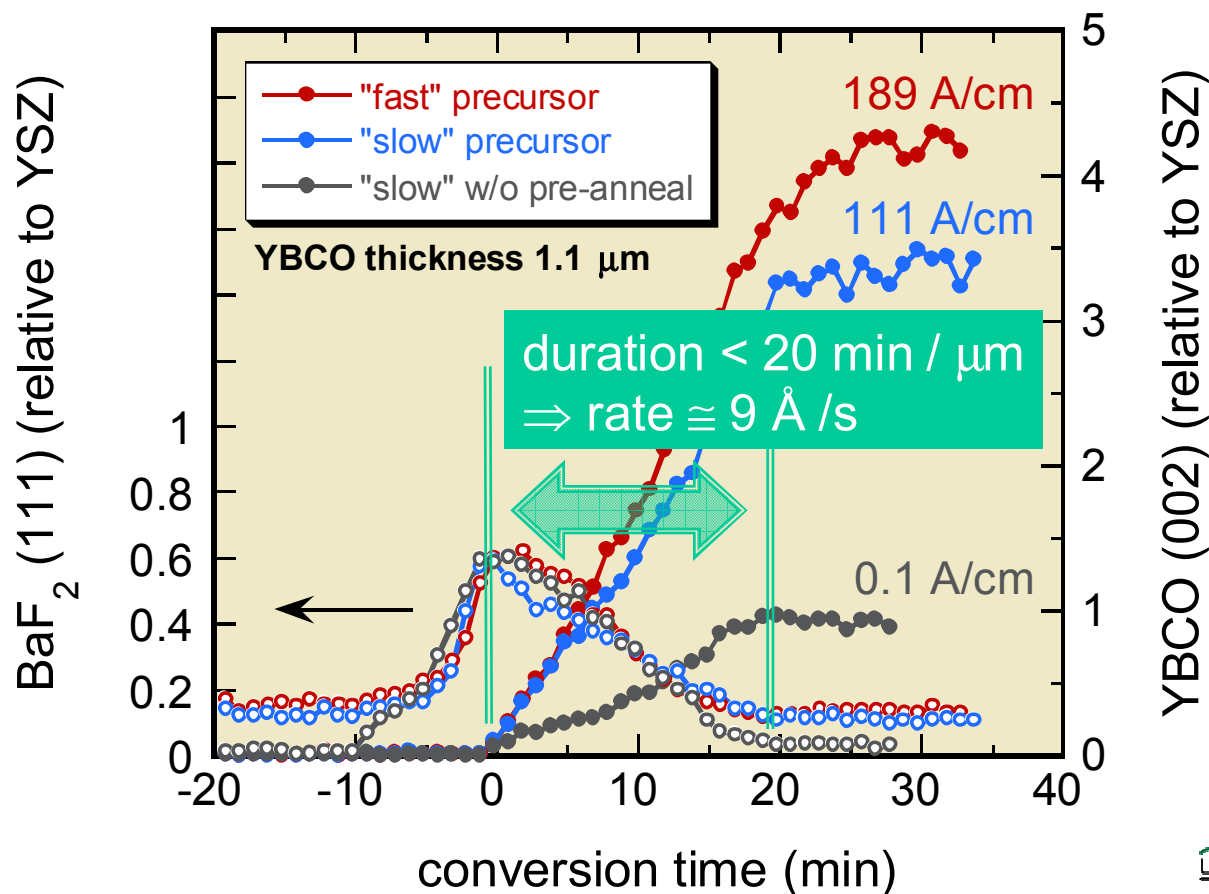
- development of the fast process
  - thickness dependent trends in  $I_c$
  - flux pinning
  - thickness dependence of  $J_c$ 
    - very thin films on RABiTS ( $d_{\min} = 15$  YBCO unit cells)
- 
- Summary of results (scoring criterion)
  - Performance and plans (scoring criterion)
  - Technology integration (scoring criterion)

# A fast conversion process was developed for PVD-BaF<sub>2</sub> precursors

- ❖ New processing scheme ties together precursor preparation history and the ex situ conversion
  - tighter control of precursor deposition conditions
  - insertion of intermediate, low-T anneal
  - “aggressive” conversion conditions (gas flow, T, p(H<sub>2</sub>O))
- ❖ Development builds on previous work:
  - review of available thick film database
  - observations during latter part of 3M-ORNL CRADA (until Fall 2002)
  - FY2003 development of “modified” process for thick YBCO
  - preliminary results (reported at 2003 Peer Review)
    - $J_c = 1.0 \text{ MA/cm}^2$  (77 K) in 0.8  $\mu\text{m}$  YBCO converted at 6 Å/s

# PVD-BaF<sub>2</sub> precursors capable of fast conversion were identified

- YBCO growth rates measured by in situ XRD (vacuum conversion)  
total pressure: 500 mTorr, YBCO area: 3 cm<sup>2</sup>

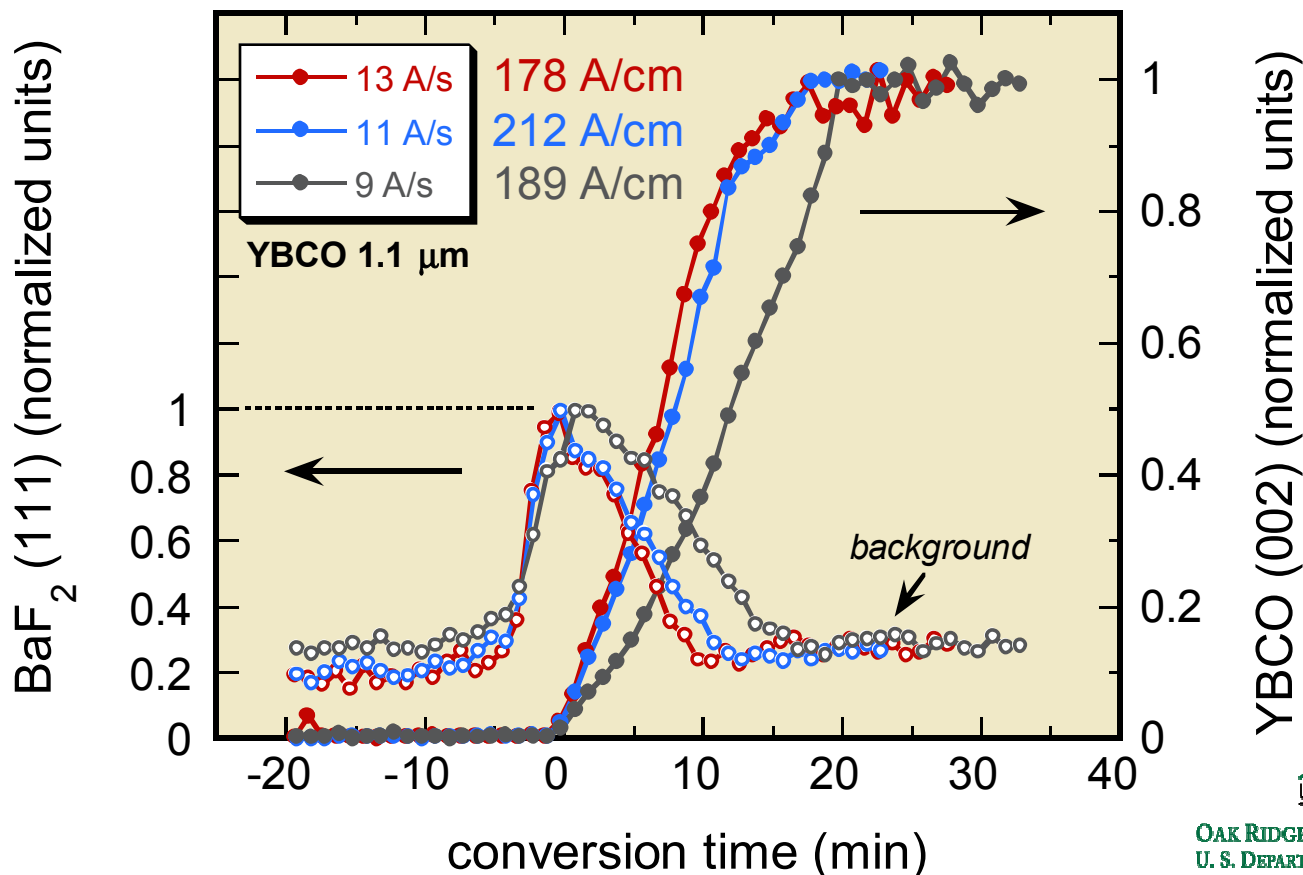




# Fast conversion process results in $I_c > 200$ A/cm at rates $>10$ Å/s (duration $< 17$ min / $\mu\text{m}$ )

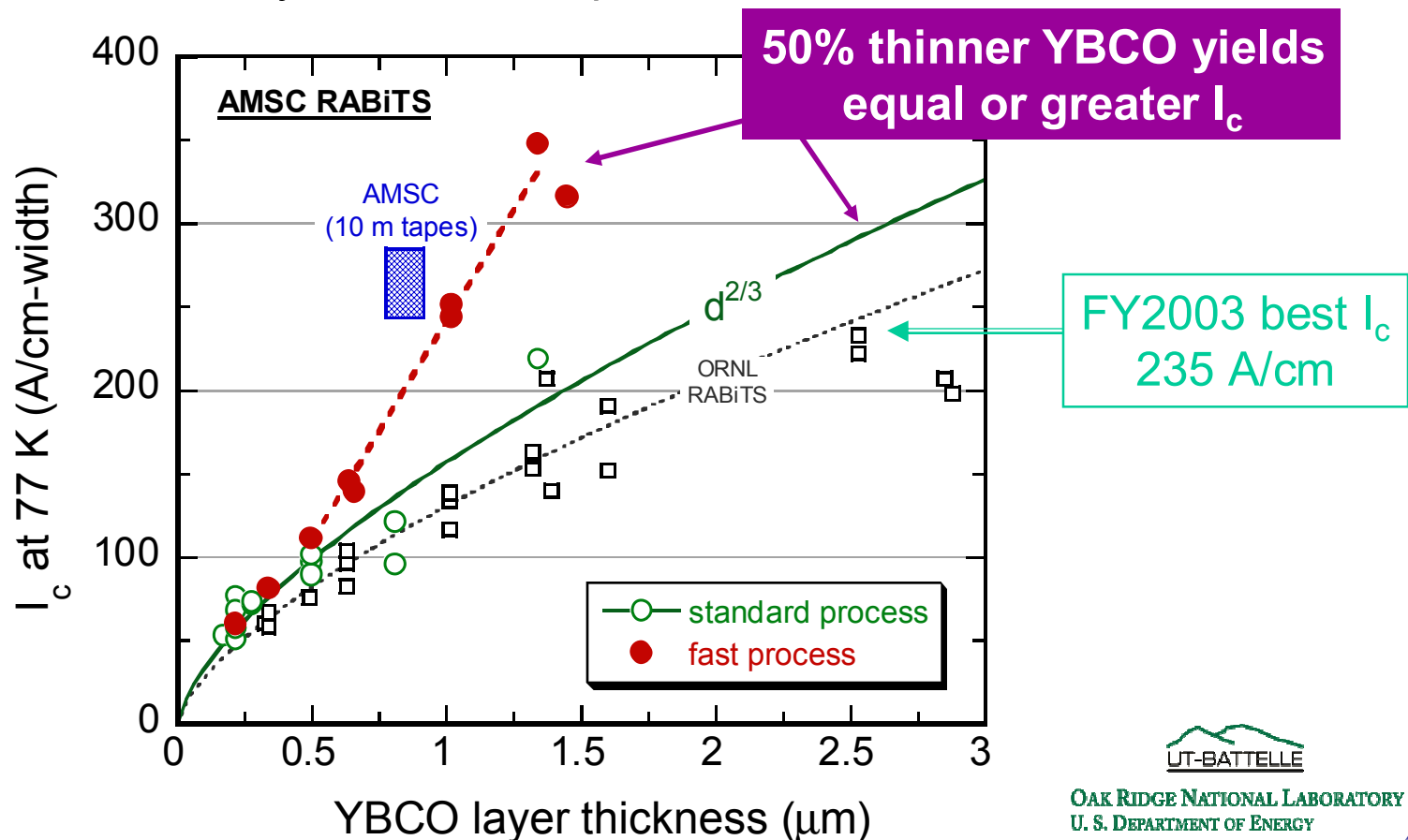
✓ FY2004 milestone of 10 Å/s has been met

- Fast conversion was also obtained in standard conversion system with flowing gas at 1 atm pressure (YBCO area:  $0.3\text{ cm}^2$ )



# $I_c$ of fast processed films increases linearly with the YBCO thickness (0.5-1.3 $\mu\text{m}$ )

- films were grown on AMSC RABiTS ( ~20% higher  $I_c$  than ORNL RABiTS)
- “standard” process yields reducing  $I_c$  increments with  $d$ :  $I_c \propto d^{2/3}$  (or  $d^{1/2}$ )
- $I_c$  determined from systematic extrapolation of  $H \leq 1$  T data



# Through-thickness imaging of fast-processed film shows a meandered GB structure

YBCO grain size is similar to substrate, constant through thickness  
 $\Rightarrow$  no bimodal structure (TEM)

original thickness:  $1.35\ \mu\text{m}$

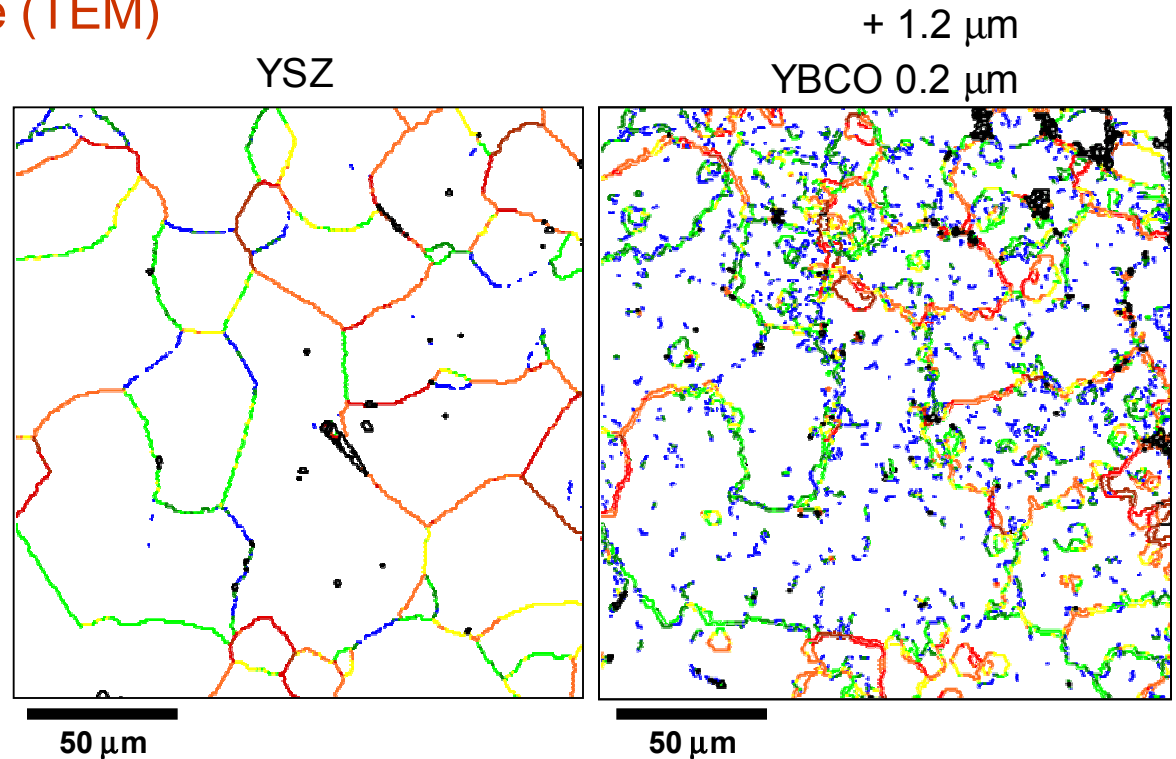
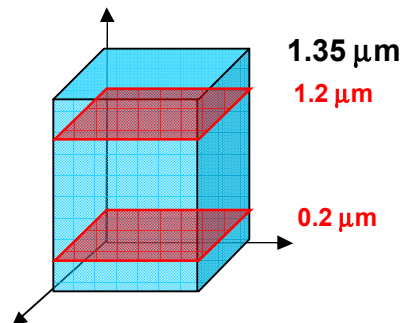
process: 29 min /  $\mu\text{m}$

$I_c = 347\ \text{A/cm}$

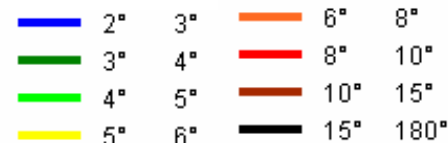
$J_c = 2.6\ \text{MA/cm}^2$



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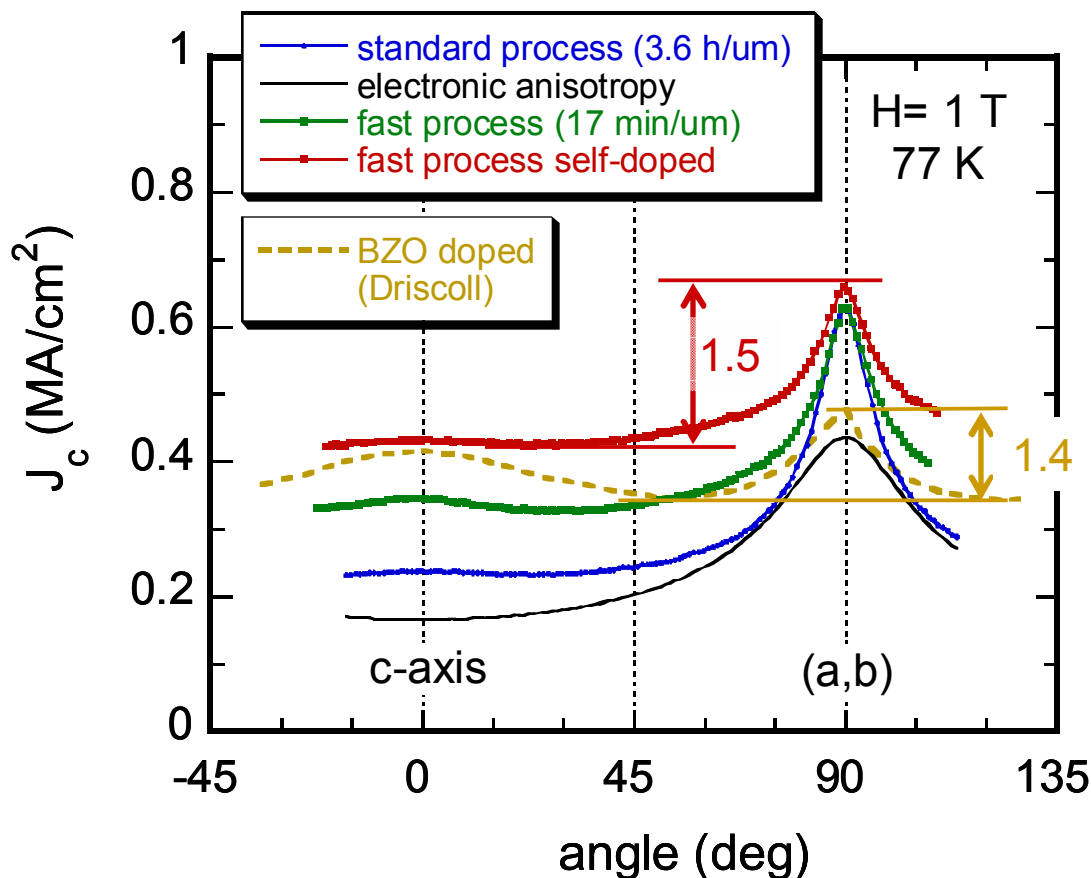


GBs color  
 coded by total  
 misorientation  
 angle ( $\theta$ ):



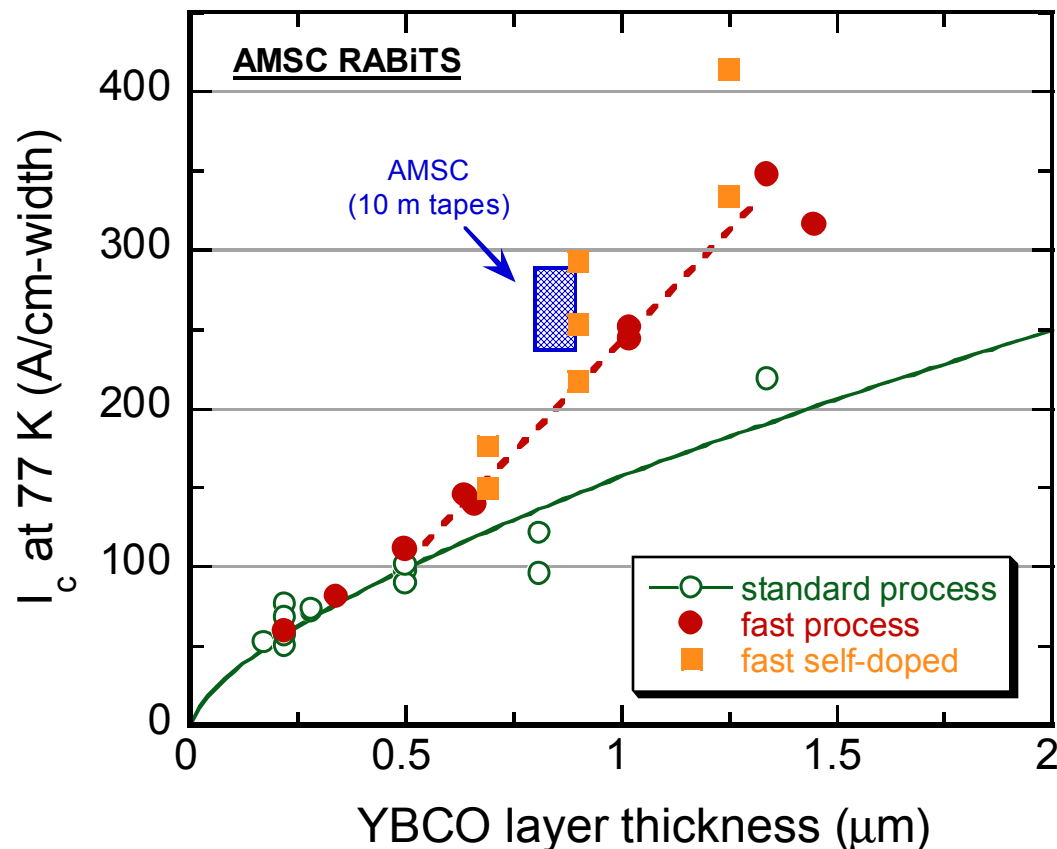
# Fast-processed films exhibit strong flux pinning and reduced field-angle anisotropy $J_c^{\max} / J_c^{\min}$

- pinning is enhanced in orientations away from (a,b)—NO peak along c
- self-doping (off-stoichiometric precursors) further enhances  $J_c$ , pinning
- pinning strengths comparable to BZO-doping were obtained



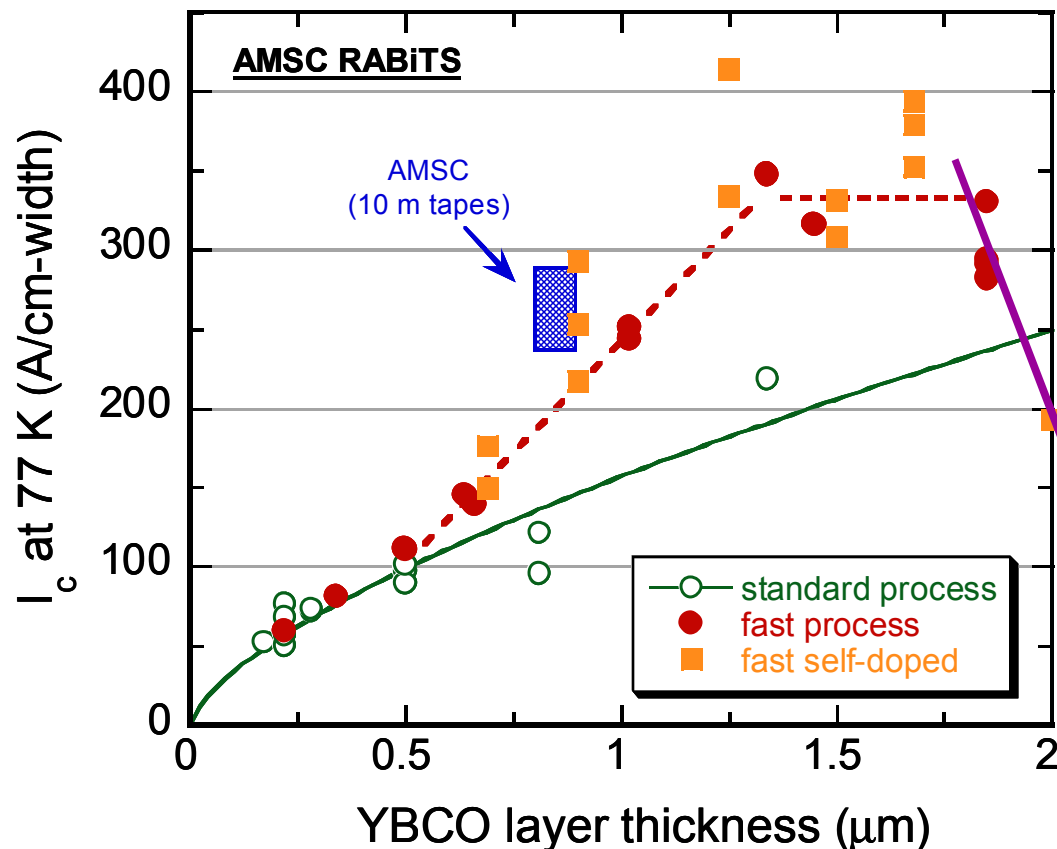
# Further $I_c$ increases resulted from self-doped (off-stoichiometric) precursors

- flux pinning study: higher  $J_c$  ( $H \parallel c$ ) from doping-induced defects
- thickness-dependent study: same  $I_c$  reached for thinner YBCO



# Linear relation between $I_c$ and YBCO thickness ceases to hold for $d > 1.3 \mu\text{m}$

- higher  $I_c$  is obtained for self-doped YBCO also for  $d > 1.3 \mu\text{m}$
- $I_c$  decreases to values less than  $I_c$  of standard process for  $d > 2 \mu\text{m}$
- new processing ideas are needed for fast conversion of thick precursors



$I_c$  decreases  
not optimized



# Through-thickness imaging of the GB network reveals probable cause of the $I_c$ -d stagnation

original YBCO thickness:  $1.85\ \mu\text{m}$

process duration: 29 min /  $\mu\text{m}$

“undoped”

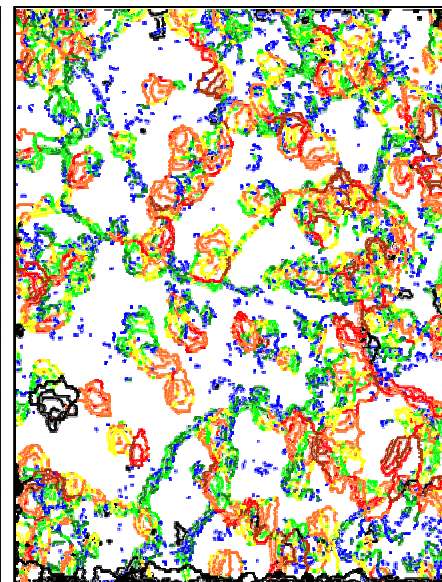
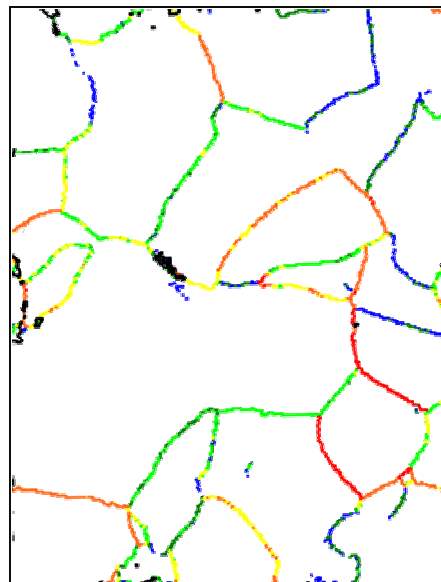
$I_c = 330\ \text{A/cm}$

$J_c = 1.8\ \text{MA/cm}^2$

+  $1.65\ \mu\text{m}$   
+  $1.25\ \mu\text{m}$   
+  $0.85\ \mu\text{m}$   
+  $0.40\ \mu\text{m}$   
+  $0.20\ \mu\text{m}$

YSZ

YBCO  $0.20\ \mu\text{m}$

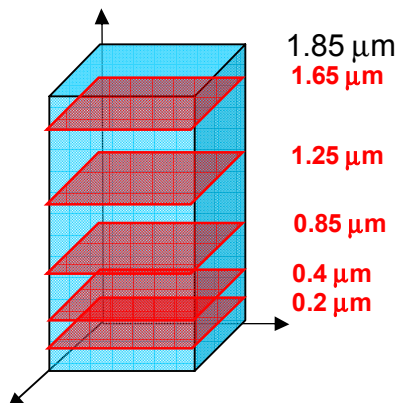


Limited overgrowth  
of substrate GBs  
⇒ moderate liquid-  
phase formation

tilted grains  
nucleate  
→ bigger  
towards the  
surface

UT-BATTELLE

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GBs color  
coded by total  
misorientation  
angle ( $\theta$ ):

2°	3°	6°	8°
3°	4°	8°	10°
4°	5°	10°	15°
5°	6°	15°	180°

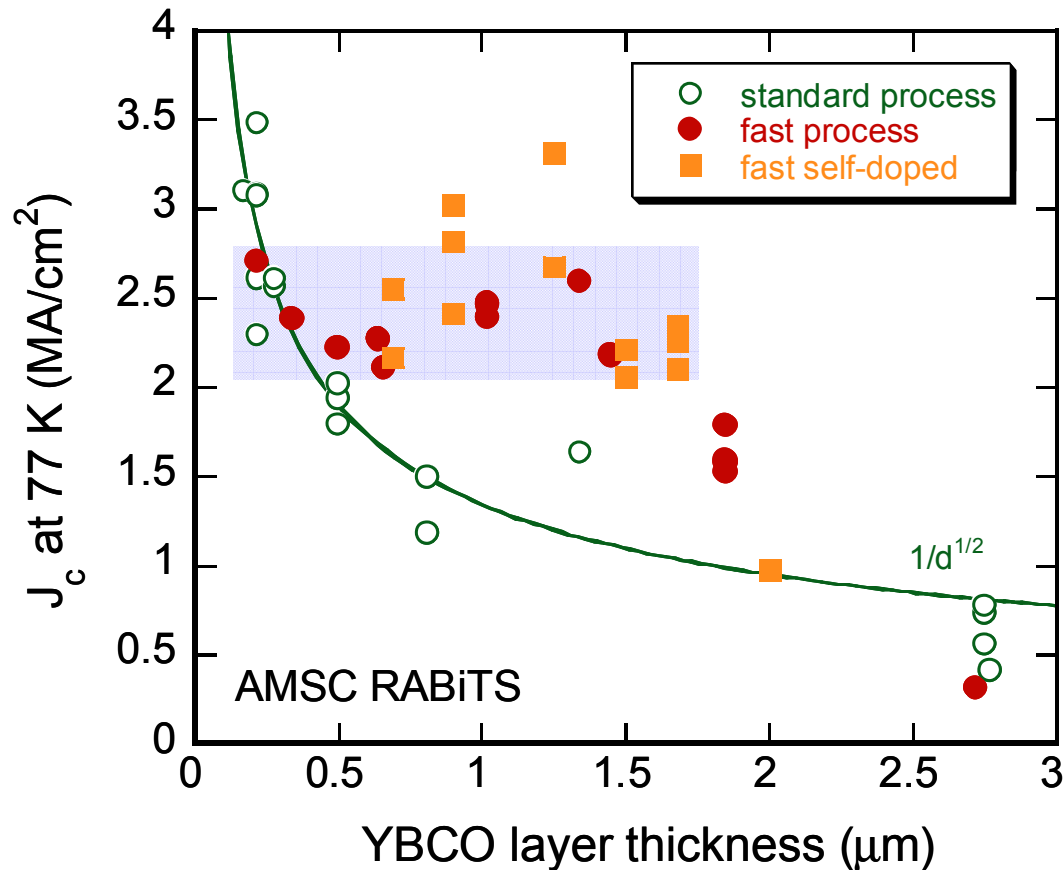


# Summary of $I_c$ results

- fast process results in high  $I_c$  values for YBCO on RABiTS
    - linear  $I_c$ -d relation in the range 0.5-1.3  $\mu\text{m}$
    - 50% less YBCO delivers same or better  $I_c$  than thick films (2.5  $\mu\text{m}$ )
  - off-stoichiometric precursors lead to self-doping effects with:
    - strong flux pinning over a wide range of magnetic field angles
    - higher  $I_c$
    - 380-410 A/cm (77K) was obtained for self-doped 1.2-1.7  $\mu\text{m}$  YBCO on AMSC RABiTS
- ✓ FY2004 milestone of 400 A/cm has been met

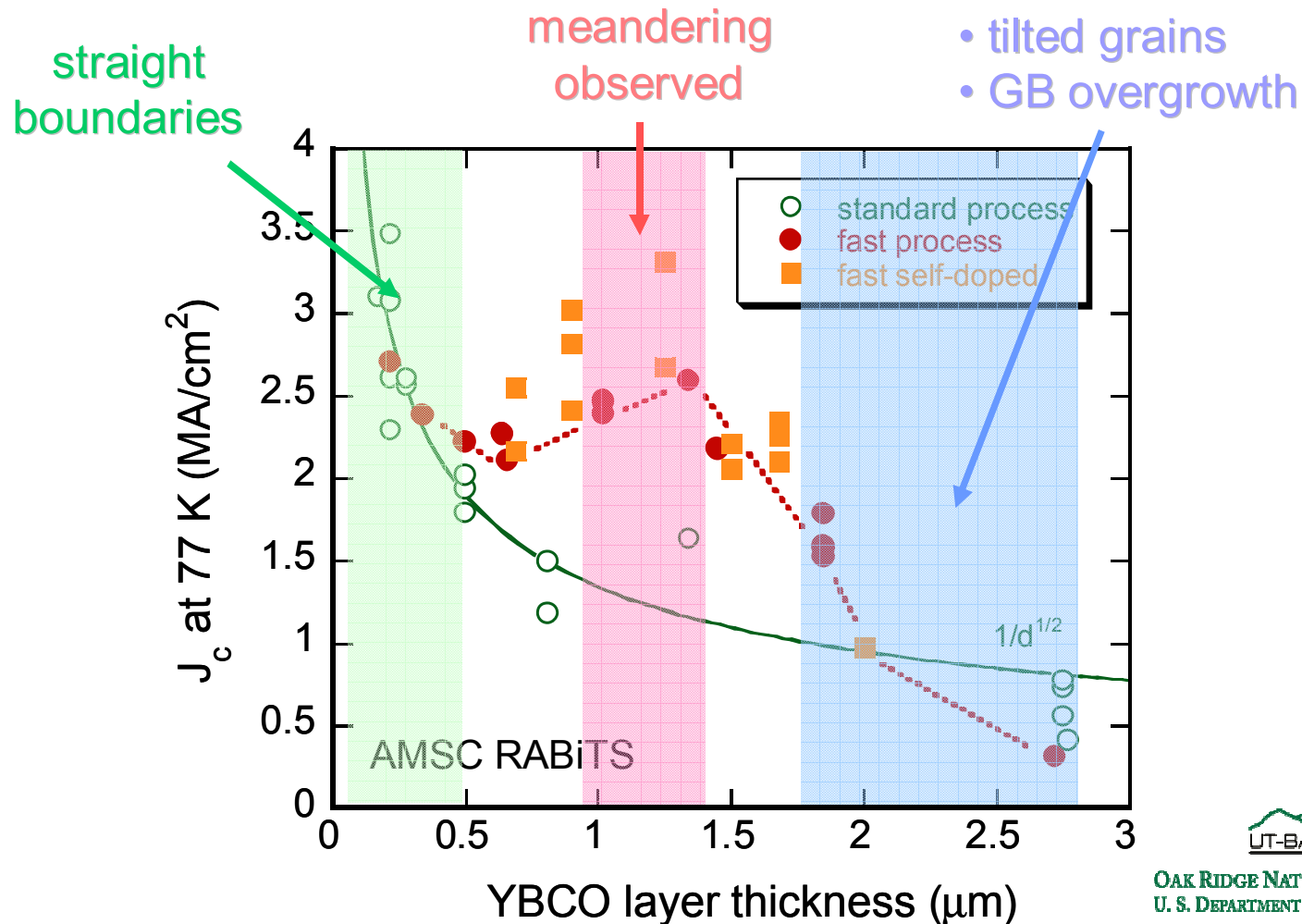
# Thickness dependence of $J_c$

# Thickness dependence of $J_c$ is drastically reduced with the fast process



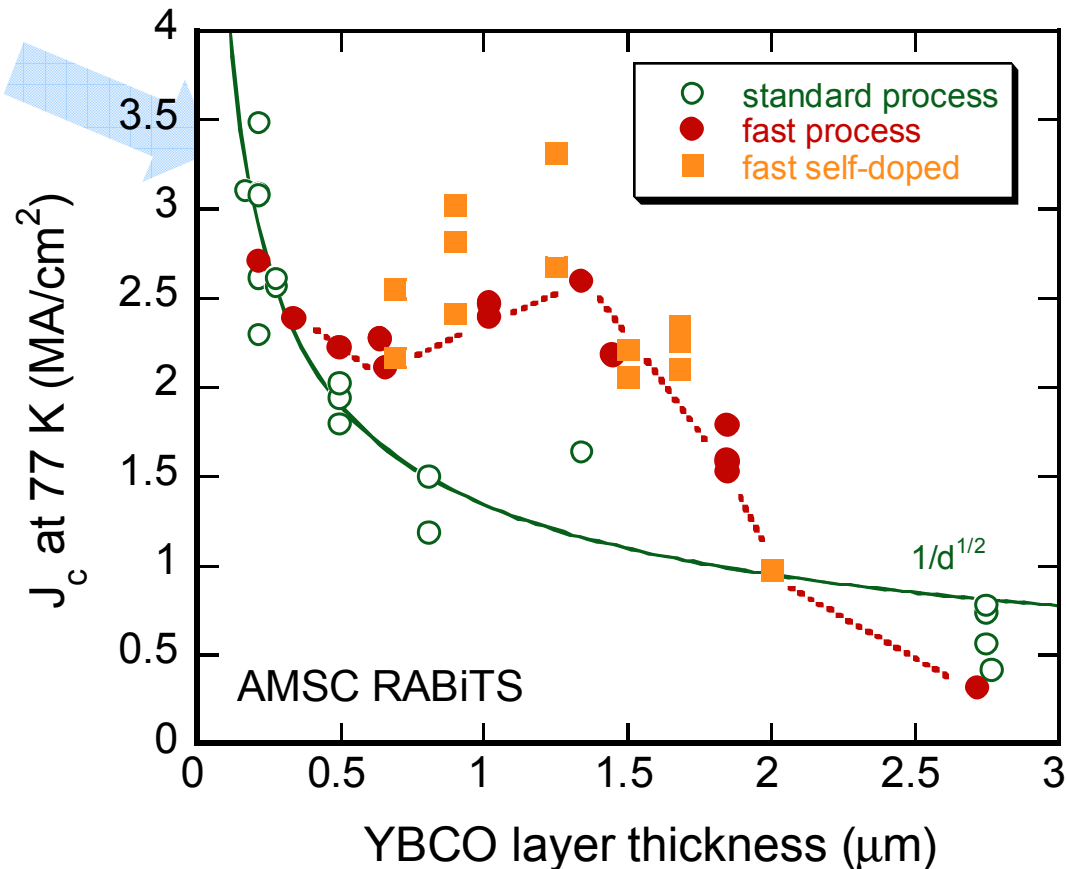
# Thickness dependence of $J_c$ exhibits an apparent “hump” for $d \cong 1\text{-}1.3\ \mu\text{m}$ (alternative interpretation)

- is the “hump” related to the “meandering” effect?



# Thickness dependence of $J_c$ exhibits an apparent “hump” for $d \cong 1\text{-}1.3\ \mu\text{m}$ (alternative interpretation)

- is the “hump” related to the “meandering” effect?  
 $\Rightarrow$  new processing opportunities to improve  $I_c$  by “GB engineering”
- what is the origin of rise in  $J_c$  for small  $d$ ?



# Study of very thin films shows a peak in $J_c$ for YBCO thickness of 0.2-0.3 $\mu\text{m}$

Anota Ijaduola and Jim Thompson (UTK) *preliminary results*

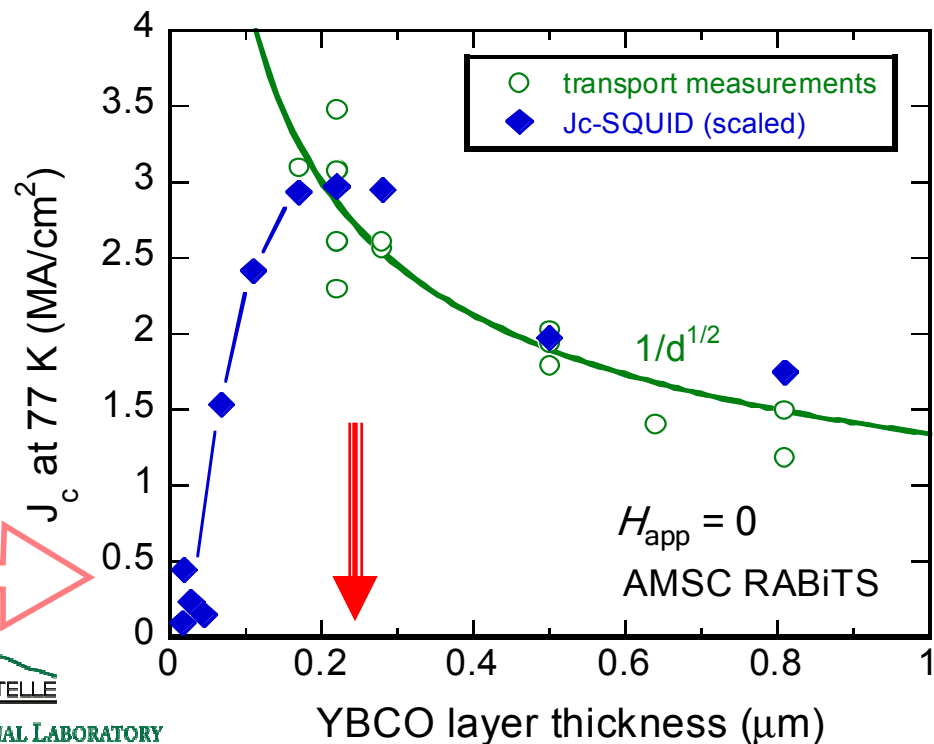
- ~consistent with earlier results of Jooss et al. for PLD YBCO on STO xtal
- thickness at peak coincides with  $(1-2) \lambda_{a,b}$  (penetration depth)  $\rightarrow$  implications ?
- data are being analyzed in collaboration with Gurevich (UW-M)

Superconducting YBCO  
< 15 unit cells thick (!)  
on metallic substrate  
(transport  $J_c$  erratic)

research supported  
by AFOSR-MURI

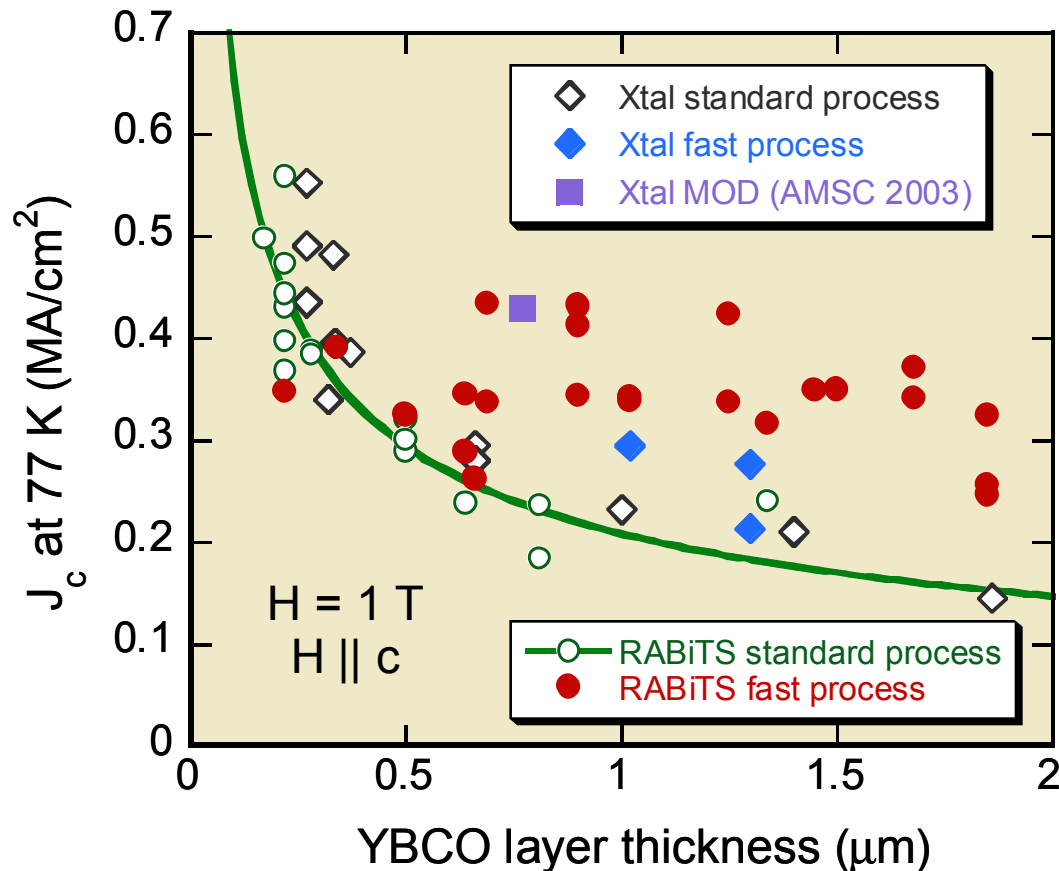


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# $J_c$ in applied field for YBCO on RABiTS exceeds available data on xtal templates

- similar to LANL observations for PLD YBCO on IBAD-MgO
- is  $J_c$  limited by GBs (at  $H = 1\text{ T}$ ,  $77\text{ K}$ ) ?
- reduced percolation effects ?





- ❑ FY2004 Results
- ❑ FY2004 Performance
- ❑ FY2005 Plans
- ❑ Technology Integration

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# FY2004 Results (Scoring Criterion)

- ❖ New processing has been developed for PVD-BaF<sub>2</sub> precursors “killing two birds with one stone”
  - conversion rates > 10 Å/s (duration < 17 min / μm-thickness)
  - fast conversion provides a vehicle for improving  $I_c$
- ❖ Properties of fast processed films:
  - linear relation between  $I_c$  and YBCO thickness (0.5-1.3 μm)
  - $I_c > 300$  A/cm for 1.3 μm YBCO on AMSC RABiTS
  - strong flux pinning with reduced field-angle anisotropy  $J_c^{\max}/J_c^{\min} < 2$
  - homogeneous, non-bimodal microstructure (1.25 μm YBCO)
- ❖ “Self-doping” (non-stoichiometric precursors) improves  $I_c$ , flux pinning, and reduces the field-angle anisotropy  $J_c^{\max}/J_c^{\min}$ 
  - $I_c \cong 400$  A/cm for 1.2-1.7 μm YBCO on AMSC RABiTS
  - at present:  $J_c$  decreases for  $d > 1.5$ -1.8 μm (*not optimized*)

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# FY2004 Results (Scoring Criterion)

- ❖ Unexpected GB structures and modifications in GB network have been visualized by through-thickness EBSD imaging
  - new observation
  - new technique, using laser marking and ion milling
- ❖ EBSD and TEM show three variants of GB network as a function of YBCO thickness (suggests a progression in the role of transient liquids)
  - $d \leq 0.5 \mu\text{m}$ —GBs are straight, in registry with substrate—minor liquid
  - $d \cong 1 \mu\text{m}$ —GBs “meander” along substrate GB—intermediate liquid
  - $d > 2 \mu\text{m}$ —complete overgrowth of substrate GBs—excessive liquid
- ❖ Alternative variant involving sub-grains observed for MOD-BaF<sub>2</sub> YBCO

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# FY2004 Results (Scoring Criterion)

- ❖ Bimodal structure in thick PVD-BaF<sub>2</sub> YBCO films correlates with  $J_c$ 
  - bimodal structure: large-grains near substrate, smaller near surface
  - interleaved secondary phases induce tilts in the smaller grains near the surface, reducing  $J_c$
  - bimodal structure without secondary phases permits high  $J_c$
  - absence of a bimodal structure in fast-processed 1.25  $\mu\text{m}$  high- $I_c$  film suggests reduced liquid phase generation
- ❖ Unique characteristics of ex situ grown YBCO films
  - laminar grain structure
  - GB meandering through-thickness / GB overgrowth
- ❖ Ubiquitous observation of pores in MOD and PVD-BaF<sub>2</sub> YBCO
  - pores are a consequence of and possibly aid the conversion process
  - pores do not inhibit the achievement of high  $I_c$

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# FY2004 Performance (Scoring Criterion)

## Goal:

Obtain 10 Å/s growth rate with PVD-BaF<sub>2</sub> precursors

## ⇒ Actions

- ✓ Developed a “fast” process that ties together precursor preparation history and conversion parameters
- ✓ Measured growth rates up to 13 Å /s by in situ XRD in a vacuum conversion system
- ✓ Produced YBCO films with  $I_c > 300$  A/cm in a standard 1-atm furnace using growth rates of 6-12 Å/s

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# FY2004 Performance (Scoring Criterion)

Goal:

Increase  $I_c$  in PVD-BaF<sub>2</sub>  
YBCO films on CC  
substrates to values  
> 400 A/cm (77K)

⇒ Actions

- ✓ Performed studies to improve processing of 1-2  $\mu\text{m}$  thick YBCO coatings on RABiTS
- ✓ Established a linear relation between  $I_c$  and YBCO thickness in fast processed films
- ✓ Applied results from flux pinning study to further improve  $I_c$ 
  - $I_c \cong 410 \text{ A/cm}$  (1.25  $\mu\text{m}$  YBCO)
  - $I_c \cong 390 \text{ A/cm}$  (1.7  $\mu\text{m}$  YBCO)

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# FY2004 Performance (Scoring Criterion)

## Goal:

Study the microstructure of PVD BaF<sub>2</sub> YBCO films by TEM to determine the role of transient liquids in the conversion process

## ⇒ Actions

- ✓ Performed analytical TEM on variable thickness films deposited on RABiTS with low and high J<sub>c</sub>
- ✓ Observed different variants of the bimodal structure in thick PVD-BaF<sub>2</sub> YBCO
- ✓ Identified secondary phase layers as a current limiting mechanism
- ✓ Compared microstructures of “standard”, “fast process”, and AMSC MOD films and identified unique characteristics of ex situ YBCO

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# FY2004 Performance (Scoring Criterion)

## Goal:

Study current limiting mechanisms in high- $I_c$  PVD and MOD-BaF<sub>2</sub> YBCO coated conductors

## ⇒ Actions

- ✓ Developed a technique to study through-thickness GB networks
- ✓ Applied the new technique to look at 3-dimensional GB networks in PVD-BaF<sub>2</sub> YBCO on RABiTS and IBAD-YSZ
- ✓ Showed that the new technique is also applicable to MOD-BaF<sub>2</sub> YBCO
- ✓ Started bi-crystal experiments to study correlations between 3-dimensional GB structures and  $J_c$

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# FY2004 Performance (Scoring Criterion)

Goal (added objective):  
Perform research in the context of the WDG to elucidate the origin of, and improve flux pinning in PVD-BaF<sub>2</sub> YBCO coated conductors

⇒ Actions

- ✓ Performed measurements of  $J_c$  as a function of H field, temperature, and field angle to build a database.
- ✓ Studied effects from variable precursor composition on flux pinning properties (“self-doping” effects)
- ❑ WDG plan to study effects of R doping in PVD-BaF<sub>2</sub> YBCO was deferred because of budgetary constraints

Goal:  
Develop a compatible buffer layer architecture for the PVD-BaF<sub>2</sub> process on IBAD-MgO template

⇒ Actions

- ❑ A limited effort was made. Needed in-depth study was deferred because of budgetary constraints

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# FY2005 Plans (Scoring Criterion)

- ❖ Study how the liquid-mediated growth can be controlled to improve the structure and properties of grain boundaries (GB) in 1-2  $\mu\text{m}$  ex situ YBCO coatings on RABiTS and IBAD templates
  - optimize  $J_c$  by variation of conversion and precursor parameters
  - use TEM and EBSD at various levels within a film to study GB structure and meandering
  - perform bi-crystal studies to relate  $J_c(\text{GB})$  to 3-dimensional variations in the GB structure
- ❖ Identify the composition of transient liquids in the conversion of PVD-BaF<sub>2</sub> precursors
  - trap liquids by quenching
  - use analytical TEM to study structure-chemistry-processing relations

*Superconductivity for Electric Systems Annual Peer Review ❖ Washington, DC ❖ July 27-29, 2004*



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# FY2005 Plans (Scoring Criterion)

- ❖ Study effects of rare-earth (R) substitutions for Y using the newly developed fast process

## Goals:

- explore new opportunities to modify the mediated growth to optimize the GB network/structure, improve  $J_c$ , flux pinning
- WDG related task
- initial studies: 100% substitution → RBCO (several R elements)
- desired direction: partial substitution → (Y,R)BCO or (R<sub>1</sub>R<sub>2</sub>)BCO
- capital investment is needed to install a fourth evaporation source in precursor deposition chamber (deferred from FY2004)
- properties will be compared to YBCO to evaluate benefits

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# Research Integration (Scoring Criterion)

- ❖ This research group represents a synergistic effort between two national laboratories, a leading university research group, and an industry leader in coated conductor research and development
- ❖ Each partner brings unique expertise to the collaboration
- ❖ Contact is maintained through frequent phone calls, email, and in-person meetings
  - WDG provides a forum to meet as a team and with AMSC
  - information from team research is shared with AMSC in a timely manner
- ❖ Interactions with other institutions leverage the research
  - ICMAB, Barcelona, Spain (thickness dependence of  $J_c^{\text{intra}}$ ,  $J_c^{\text{inter}}$ )
    - 2 Spanish students at ORNL last summer
  - NIST-Gaithersburg (phase development)
  - NIST-Boulder (strain effects: thick YBCO on RABiTS)

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# Thanks !

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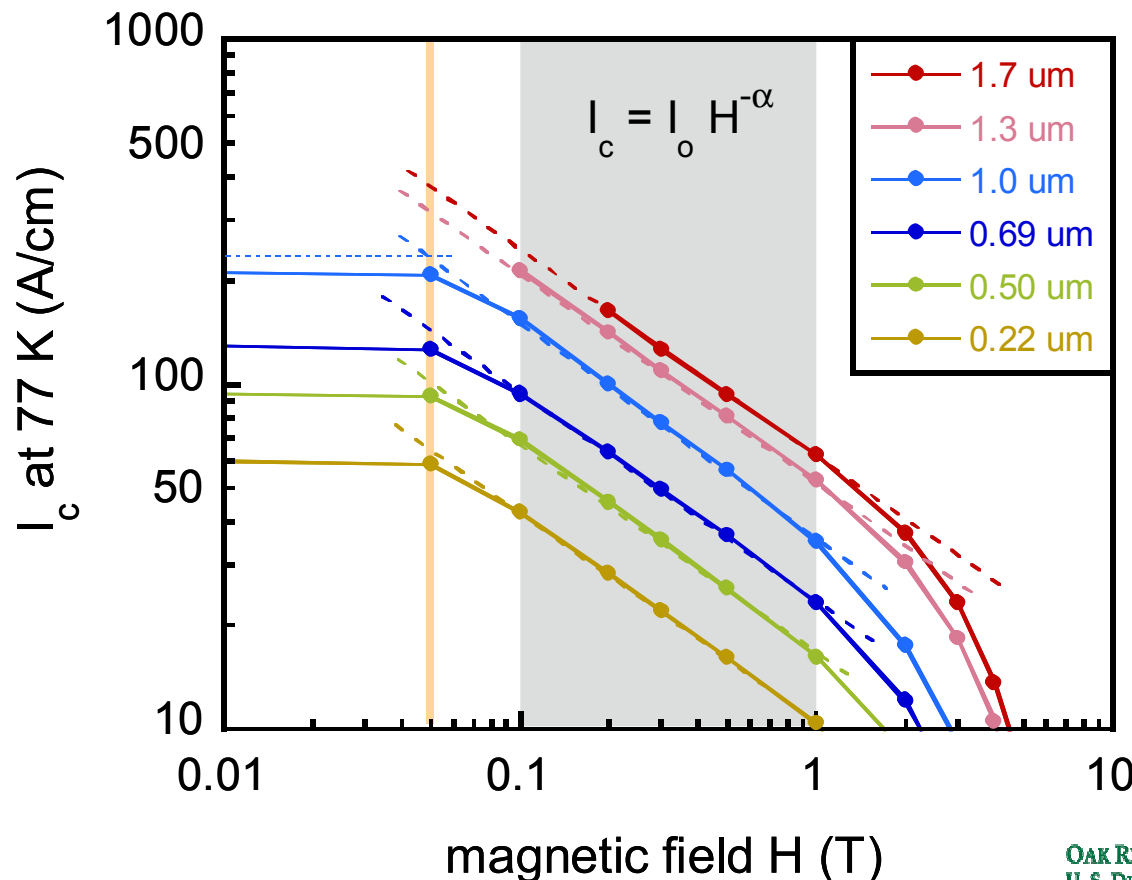
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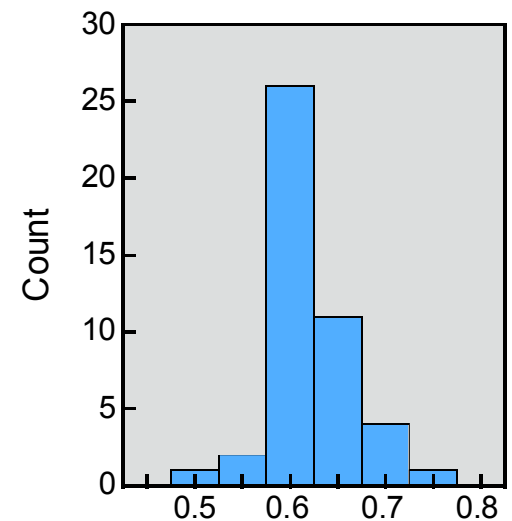
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# $I_c$ increases with YBCO thickness over a wide range of applied magnetic fields

Use extrapolation of linear  $I_c(H)$  dependence in log-log representation to estimate  $I_c(0)$  of thick films (beyond experimental range)



exponent  $\alpha \cong 0.6$   
for most films



# Log-log extrapolation provides a meaningful estimate of self-field $I_c$ beyond measurement range

- robust demonstration of  $I_c(0) > 350$  A/cm ( $d \cong 1.2$ - $1.7$   $\mu\text{m}$ )
- approach is more systematic than conversion from single  $I_c(H)$  value

